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Environmental Soil Chemistry: An Overview

Soil chemistry is the branch of soil science that deals with the chemical composition, chemical properties, and chemical reactions of soils. Soils are heterogeneous mixtures of air, water, inorganic and organic solids, and microorganisms (both plant and animal in nature). Soil chemistry is concerned with the chemical reactions involving these phases. For example, carbon dioxide in the air combined with water acts to weather the inorganic solid phase. Chemical reactions between the soil solids and the soil solution influence both plant growth and water quality.

Soil chemistry has traditionally focused on the chemical reactions in soils that affect plant growth and plant nutrition. However, beginning in the 1970s and certainly in the 1990s, as concerns increased about inorganic and organic contaminants in water and soil and their impact on plant, animal, and human health, the emphasis of soil chemistry is now on environmental soil chemistry. Environmental soil chemistry is the study of chemical reactions between soils and environmentally important plant nutrients, radionuclides, metals, metalloids, and organic chemicals. These water and soil contaminants will be discussed later in this chapter.

A knowledge of environmental soil chemistry is fundamental in predicting the fate of contaminants in the surface and subsurface environments. An understanding of the chemistry and mineralogy of inorganic and organic soil components is necessary to comprehend the array of chemical reactions that contaminants may undergo in the soil environment. These reactions, which may include equilibrium and kinetic processes such as dissolution, precipitation, polymerization, adsorption/desorption, and oxidation–reduction, affect the solubility, mobility, speciation (form), toxicity, and bioavailability of contaminants in soils and in surface waters and groundwaters. A knowledge of environmental soil chemistry is also useful in making sound and cost effective decisions about remediation of contaminated soils.

Evolution of Soil Chemistry

Soil chemistry, as a subdiscipline of soil science, originated in the early 1850s with the research of J. Thomas Way, a consulting chemist to the Royal Agricultural Society in England. Way, who is considered the father of soil chemistry, carried out a remarkable group of experiments on the ability of soils to exchange ions. He found that soils could adsorb both cations and anions, and that these ions could be exchanged with other ions. He noted that ion exchange was rapid, that clay was an important soil component in the adsorption of cations, and that heating soils or treating them with strong acid decreased the ability of the soils to adsorb ions. The vast majority of Way's observations were later proven correct, and his work laid the groundwork for many seminal studies on ion exchange and ion sorption that were later conducted by soil chemists. Way's studies also had immense impact on other disciplines including chemical engineering and chemistry. Research on ion exchange has truly been one of the great hallmarks of soil chemistry (Sparks, 1994).

The forefather of soil chemistry in the United States was Edmund Ruffin, a philosopher, rebel, politician, and farmer from Virginia. Ruffin fired the first Confederate shot at Fort Sumter, South Carolina. He committed suicide after Appomattox because he did not wish to live under the "perfidious Yankee race." Ruffin was attempting to farm near Petersburg, Virginia, on soil that was unproductive. He astutely applied oyster shells to his land for the proper reason—to correct or ameliorate soil acidity. He also accurately described zinc deficiencies in his journals (Thomas, 1977).

Much of the research in soil chemistry between 1850 and 1900 was an extension of Way's work. During the early decades of the 20th century classic ion exchange studies by Gedroiz in Russia, Hissink in Holland, and Kelley and Vanselow in California extended the pioneering investigations and conclusions of Way. Numerous ion exchange equations were developed to explain and predict binary reactions (reactions involving two ions) on clay minerals and soils. These were named after the scientists who developed them and included the Kerr, Vanselow, Gapon, Schofield, Krishnamoorthy and Overstreet, Donnan, and Gaines and Thomas equations.

Linus Pauling (1930) conducted some classic studies on the structure of layer silicates that laid the foundation for extensive studies by soil chemists and mineralogists on clay minerals in soils. A major discovery was made by Hendricks and co-workers (Hendricks and Fry, 1930) and Kelley and co-workers (1931) who found that clay minerals in soils were crystalline. Shortly thereafter, X-ray studies were conducted to identify clay minerals and to determine their structures. Immediately, studies were carried out to investigate the retention of cations and anions on clays, oxides, and soils, and mechanisms of retention were proposed. Particularly noteworthy were early studies conducted by Schofield and Samson (1953) and Mehlich (1952), who validated some of Sante Mattson's earlier theories on sorption phenomena (Mattson, 1928). These studies were the forerunners of another important theme in soil chemistry research: surface chemistry of soils.

One of the most interesting and important bodies of research in soil chemistry has been the chemistry of soil acidity. As Hans Jenny so eloquently wrote, investigations on soil acidity were like a merry-go-round. Fierce arguments ensued about whether acidity was primarily attributed to hydrogen or aluminum and were the basis for many studies during the past century. It was Coleman and Thomas (1967) and Rich and co-workers (Rich and Obenshain, 1955; Hsu and Rich, 1960) who, based on numerous studies, concluded that aluminum, including trivalent, monomeric (one Al ion), and polymeric (more than one Al ion) hydroxy, was the primary culprit in soil acidity.

Studies on soil acidity, ion exchange, and retention of ions by soils and soil components such as clay minerals and hydrous oxides were major research themes of soil chemists for many decades.

Since the 1970s studies on rates and mechanisms of heavy metal, oxyanion, radionuclide, pesticide, and other organic chemical interactions with soils and soil components (see Chapters 5 and 7); the effect of mobile colloids on the transport of pollutants; the environmental chemistry of aluminum in soils, particularly acid rain effects on soil chemical processes (see Chapter 9); oxidation–reduction (see Chapter 8) phenomena involving soils and inorganic and organic contaminants; and chemical interactions of sludges (biosolids), manures, and industrial by-products and coproducts with soils have been prevalent research topics in environmental soil chemistry.

The Modern Environmental Movement

To understand how soil chemistry has evolved from a traditional emphasis on chemical reactions affecting plant growth to a focus on soil contaminant reactions, it would be useful to discuss the environmental movement.

The modern environmental movement began over 30 years ago when the emphasis was on reducing pollution from smokestacks and sewer pipes. In the late 1970s a second movement that focused on toxic compounds was initiated. During the past few decades, several important laws that have had a profound influence on environmental policy in the United States were enacted. These are the Clean Air Act of 1970, the Clean Water Act of 1972, the Endangered Species Act, the Superfund Law of 1980 for remediating contaminated toxic waste sites, and the amended Resource Conservation and Recovery Act (RCRA) of 1984, which deals with the disposal of toxic wastes.

The third environmental wave, beginning in the late 1980s and orchestrated by farmers, businesses, homeowners, and others, is questioning the regulations and the often expensive measures that must be taken to satisfy these regulations. Some of the environmental laws contain regulations that some pollutants cannot be contained in the air, water, and soil at levels greater than a few parts per billion. Such low concentrations can be measured only with very sophisticated analytical equipment that was not available until only recently.

Critics are charging that the laws are too rigid, impose exorbitant cost burdens on the industry or business that must rectify the pollution problem, and were enacted based on emotion and not on sound scientific data. Moreover, the critics charge that because these laws were passed without the benefit of careful and thoughtful scientific studies that considered toxicological and especially epidemiological data, the risks were often greatly exaggerated and unfounded, and cost–benefit analyses were not conducted.

Despite the questions that have ensued concerning the strictness and perhaps the inappropriateness of some of the regulations contained in environmental laws, the fact remains that the public is very concerned about the quality of the environment. They have expressed an overwhelming willingness to spend substantial tax dollars to ensure a clean and safe environment.

Contaminants in Waters and Soils

There are a number of inorganic and organic contaminants that are important in water and soil. These include plant nutrients such as nitrate and phosphate; heavy metals such as cadmium, chromium, and lead; oxyanions such as arsenite, arsenate, and selenite; organic chemicals; inorganic acids; and radionuclides. The sources of these contaminants include fertilizers, pesticides, acidic deposition, agricultural and industrial waste materials, and radioactive fallout. Discussions on these contaminants and their sources are provided below. Later chapters will discuss the soil chemical reactions that these contaminants undergo and how a knowledge of these reactions is critical in predicting their effects on the environment.

Water Quality

Pollution of surface water and groundwater is a major concern throughout the world. There are two basic types of pollution—*point* and *nonpoint*. Point pollution is contamination that can be traced to a particular source such as an industrial site, septic tank, or wastewater treatment plant. Nonpoint pollution results from large areas and not from any single source and includes both natural and human activities. Sources of nonpoint pollution include agricultural, human, forestry, urban, construction, and mining activities and atmospheric deposition. There are also naturally occurring nonpoint source pollutants that are important. These include geologic erosion, saline seeps, and breakdown of minerals and soils that may contain large quantities of nutrients. Natural concentrations of an array of inorganic species in groundwater are shown in Table 1.1.

To assess contamination of ground and surface waters with plant nutrients such as N and P, pesticides, and other pollutants a myriad of interconnections including geology, topography, soils, climate and atmospheric inputs, and human activities related to land use and land management practices must be considered (Fig. 1.1).

Perhaps the two plant nutrients of greatest concern in surface and groundwater are N and P. The impacts of excessive N and P on water quality, which can affect both human and animal health, have received increasing attention. The U.S. EPA has established a maximum contaminant level (MCL) of 10 mg liter^{-1} nitrate as N for groundwater. It also established a goal that total phosphate not exceed 0.05 mg liter^{-1} in a stream where it enters a lake or reservoir and that total P in streams that do not discharge directly to lakes or reservoirs not exceed 0.1 mg liter^{-1} (EPA, 1987).

Excessive N and P can cause eutrophication of water bodies, creating excessive growth of algae and other problematic aquatic plants. These plants can clog water pipes and filters and impact recreational endeavors such as fishing, swimming, and boating. When algae decays, foul odors, obnoxious tastes, and low levels of dissolved oxygen in water (hypoxia) can result. Excessive nutrient concentrations have been linked to hypoxia conditions in the Gulf of Mexico, causing harm to fish and shellfish, and to the growth of the dinoflagellate *Pfisteria*, which has been found in Atlantic Coastal Plain waters. Recent outbreaks of *Pfisteria* have been related to fish kills and toxicities to humans (USGS, 1999). Excessive N, in the form of nitrates, has been linked to methemoglobinemia or blue baby syndrome, abortions in women (Centers for Disease Control and Prevention, 1996), and increased risk of non-Hodgkin's lymphoma (Ward *et al.,* 1996).

Phosphorus, as phosphate, is usually not a concern in groundwater, since it is tenaciously held by soils through both electrostatic and nonelectrostatic mechanisms (see Chapter 5 for definitions and discussions) and usually does not leach in most soils. However, in sandy soils that contain little clay, Al or Fe oxides, or organic matter, phosphate can leach through the soil and impact groundwater quality. Perhaps the greatest concern with phosphorus is con-

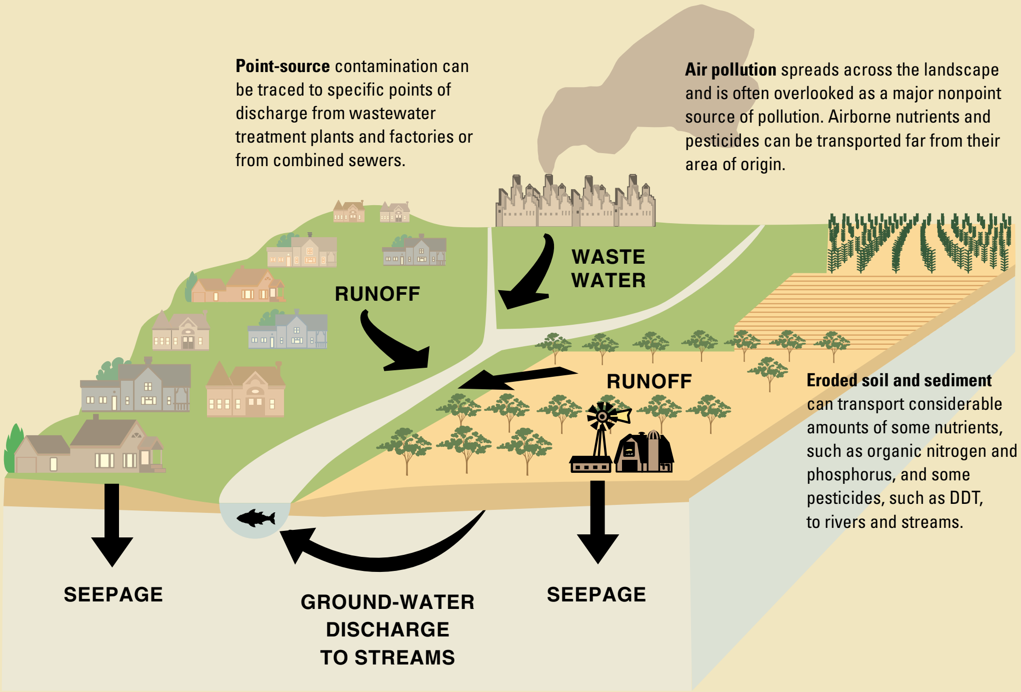
TABLE 1.1. *Natural Concentrations of Various Elements, Ions, and Compounds in Groundwater*[a,b]

	Concentration			Concentration	
Element	Typical value	Extreme value	Element	Typical value	Extreme value
	Major Elements (mg liter^{-1})		Bi	< 20	
Ca	1.0–150^c	95,000^d	Br	< 100–2,000	
	< 500^c		Cd	< 1.0	
Cl	1.0–70^c	200,000^d	Co	<10	
	< 1,000^e		Cr	< 1.0–5.0	
F	0.1–5.0	70	Cu	< 1.0–3.0	
		1,600^d	Ga	< 2.0	
Fe	0.01–10	> 1,000^{d,f}	Ge	< 20–50	
K	1.0–10	25,000^d	Hg	< 1.0	
Mg	1.0–50^c	52,000^d	I	< 1.0–1,000	48^d
	< 400^e		Li	1.0–150	
Na	0.5–120^c	120,000^d	Mn	< 1.0–1,000	10^b
	< 1,000^e		Mo	< 1.0–30	10
NO_3	0.2–20	70	Ni	< 10–50	
SiO_2	5.0–100	4,000^d	PO_4	< 100–1,000	
SO_4	3.0–150^c	200,000^d	Pb	< 15	
	< 2,000^e		Ra	< 0.1–4.0^g	0.7^{d,g}
Sr	0.1–4.0	50	Rb	< 1.0	
	Trace Elements (mg liter^{-1})		Se	< 1.0–10	
Ag	< 5.0		Sn	< 200	
Al	< 5.0–1,000		Ti	< 1.0–150	
As	< 1.0–30	4	U	0.1–40	
B	20–1,000	5	V	< 1.0–10	0.07
Ba	10–500		Zn	< 10–2,000	
Be	< 10		Zr	< 25	

[a] From Dragun (1988).
[b] Based on an analysis of data presented in Durfer and Becker (1964), Hem (1970), and Ebens and Schaklette (1982).
[c] In relatively humid regions.
[d] In brine.
[e] In relatively dry regions.
[f] In thermal springs and mine areas.
[g] Picocuries liter^{-1} (i.e., 0.037 disintegrations sec^{-1}).

tamination of streams and lakes via surface runoff and erosion. Nitrate-N is weakly held by soils and readily leaches in soils. Contamination of groundwater with nitrates is a major problem in areas that have sandy soils.

Major sources of N and P in the environment are inorganic fertilizers, animal manure, biosolid applications, septic systems, and municipal sewage systems. Inorganic N and P fertilizers increased 20- and 4-fold, respectively, between 1945 and the early 1980s and leveled off thereafter (Fig. 1.2). In 1993, ~12 million metric tons of N and 2 million metric tons of P were used nationwide. At the same time, animal manure accounted for ~7 million metric tons of N and about 2 million metric tons of P. Additionally, about 3 million metric tons of N per year are derived from atmospheric sources (Puckett, 1995).



Point-source contamination can be traced to specific points of discharge from wastewater treatment plants and factories or from combined sewers.

Air pollution spreads across the landscape and is often overlooked as a major nonpoint source of pollution. Airborne nutrients and pesticides can be transported far from their area of origin.

Eroded soil and sediment can transport considerable amounts of some nutrients, such as organic nitrogen and phosphorus, and some pesticides, such as DDT, to rivers and streams.

Fish and other aquatic organisms reflect cumulative effects of water chemistry and land-use activities. Fish, for example, acquire some pesticides by ingesting stream invertebrates or smaller fish that have fed on contaminated plants. Fish also can accumulate some contaminants directly from water passing over their gills.

Ground water—the unseen resource—is the source of drinking water for more than 50 percent of the Nation. As water seeps through the soil, it carries with it substances applied to the land, such as fertilizers and pesticides. Water moves through water-bearing formations, known as aquifers, and eventually surfaces in discharge areas, such as streams, lakes, and estuaries. It is common to think of surface water and ground water as separate resources; however, they are interconnected. Ground-water discharge can significantly affect the quality and quantity of streams, especially during low-flow conditions. Likewise, surface water can affect the quality and quantity of ground water.

FIGURE 1.1. *Interactions between surface and groundwater, atmospheric contributions, natural landscape features, human activities, and aquatic health and impacts on nutrients and pesticides in water resources. From U.S. Geological Survey, Circular 1225, 1999.*

Pesticides

Pesticides can be classified as herbicides, those used to control weeds, insecticides, to control insects, fungicides, to control fungi, and others such as nematicides and rodenticides.

Pesticides were first used in agricultural production in the second half of the 19th century. Examples included lead, arsenic, copper, and zinc salts, and naturally produced plant compounds such as nicotine. These were used for insect and disease control on crops. In the 1930s and 1940s 2,4-D, an herbicide, and DDT, an insecticide, were introduced; subsequently, increasing amounts of pesticides were used in agricultural production worldwide.

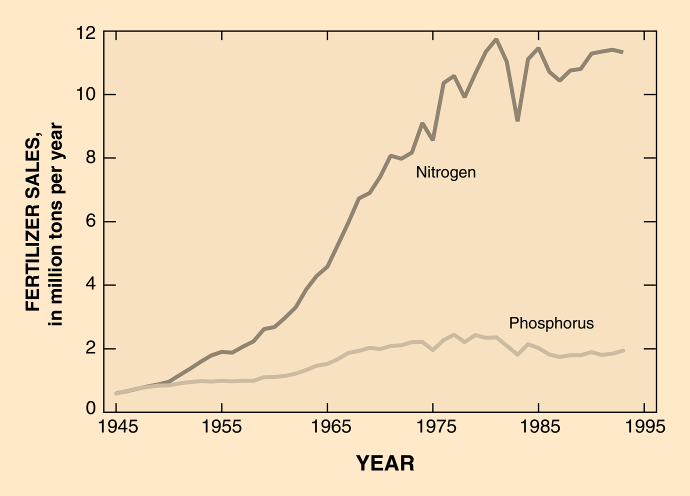


FIGURE 1.2. *Changes in nitrogen and fertilizer use over the decades. From U.S. Geological Survey, Circular 1225, 1999.*

The benefits that pesticides have played in increasing crop production at a reasonable cost are unquestioned. However, as the use of pesticides increased, concerns were expressed about their appearance in water and soils, and their effects on humans and animals. Total pesticide use in the United States has stayed constant at about 409 million kg per year after increasing significantly through the mid-1970s due to greater herbicide use (Fig. 1.3). Agriculture accounts for 70–80% of total pesticide use. About 60% of the agricultural use of pesticides involves herbicide applications.

One of the most recent and comprehensive assessments of water quality in the United States has been conducted by the USGS through its National Water Quality Assessment (NAWQA) Program (USGS, 1999). This program is assessing water quality in more than 50 major river basins and aquifer systems. These include water resources provided to more than 60% of the U.S. population in watersheds that comprise about 50% of the land area of the conterminous United States. Figure 1.4 shows 20 of the systems that were evaluated beginning in 1991, and for which data were recently released (USGS, 1999). Water quality patterns were related to chemical use, land use, climate, geology, topography, and soils.

The relative level of contamination of streams and shallow groundwater with N, P, herbicides, and insecticides in different areas is shown in Fig. 1.5. There is a clear correlation between contamination level and land use and the amounts of nutrients and chemical used.

Nitrate levels were not a problem for humans drinking water from streams or deep aquifers. However, about 15% of all shallow groundwater sampled below agricultural and urban areas exceeded the MCL for NO_3^-. Areas that ranked among the highest 25% of median NO_3^- concentration in shallow groundwaters were clustered in the mid-Atlantic and Western parts of the

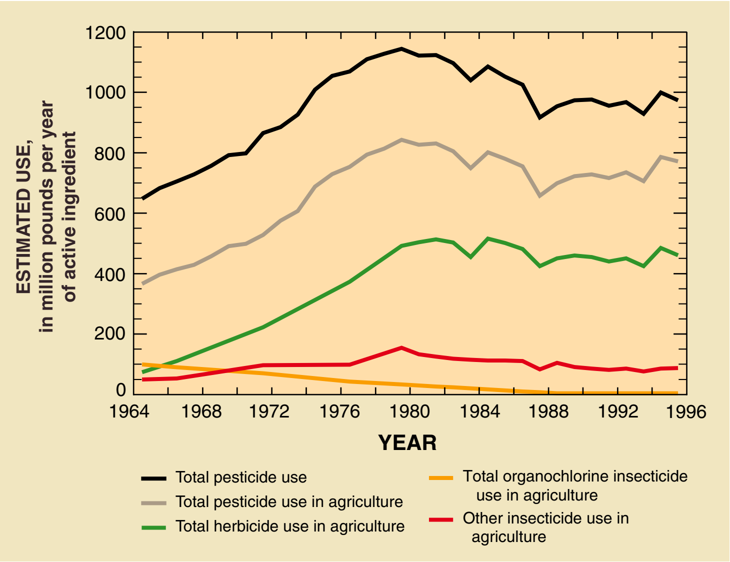


FIGURE 1.3. *Changes in agricultural pesticide use over the decades. From U.S. Geological Survey, Circular 1225, 1999.*

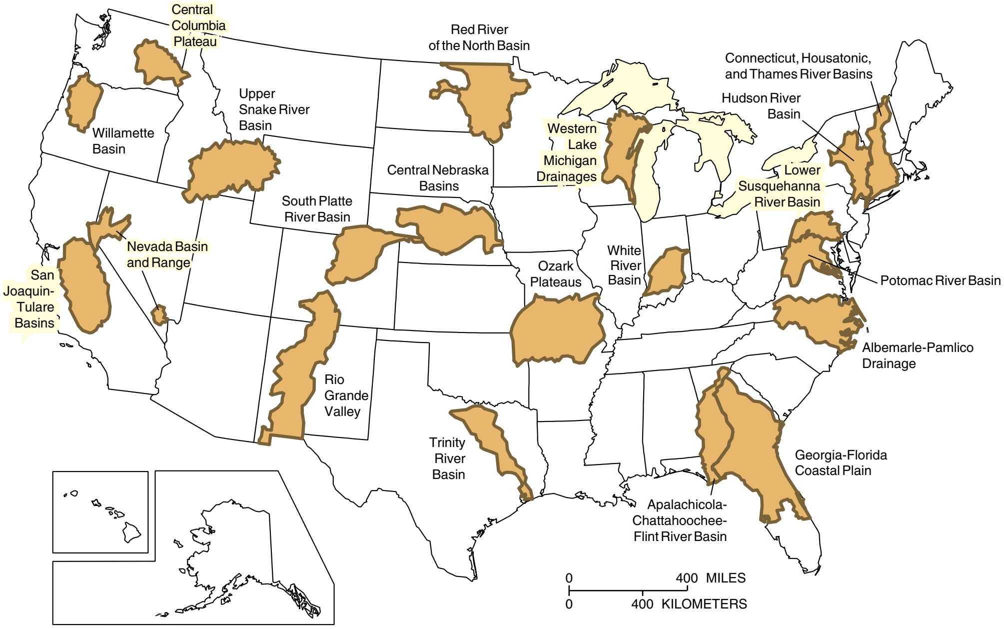
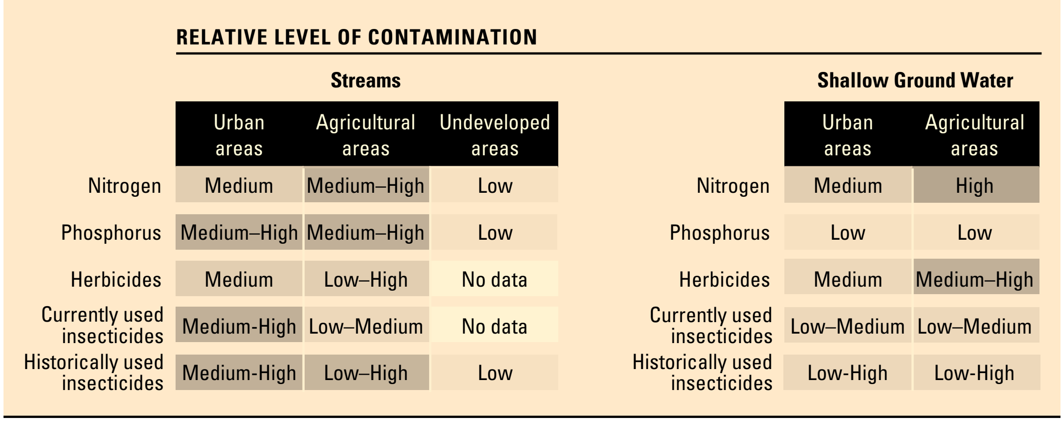


FIGURE 1.4. *Locations of wells sampled as part of NAWQA land-use studies and major aquifer survey conducted during 1992–1995. From U.S. Geological Survey, Circular 1225, 1999.*



RELATIVE LEVEL OF CONTAMINATION

	Streams			Shallow Ground Water	
	Urban areas	Agricultural areas	Undeveloped areas	Urban areas	Agricultural areas
Nitrogen	Medium	Medium–High	Low	Medium	High
Phosphorus	Medium–High	Medium–High	Low	Low	Low
Herbicides	Medium	Low–High	No data	Medium	Medium–High
Currently used insecticides	Medium-High	Low–Medium	No data	Low–Medium	Low–Medium
Historically used insecticides	Medium-High	Low–High	Low	Low-High	Low-High

FIGURE 1.5. *Levels of nutrients and pesticides in streams and shallow groundwater and relationship to land use. From U.S. Geological Survey, Circular 1225, 1999.*

United States (Fig. 1.6). These findings are representative of differences in N loading, land use, soil and aquifer permeability, irrigation practices, and other factors (USGS, 1999).

Total P concentrations in agricultural streams were among the highest measured and correlated with nonpoint P inputs. The highest total P levels in urban streams were in densely populated areas of the arid Western and of the Eastern United States.

The NAWQA studies showed that pesticides were prevalent in streams and groundwater in urban and agricultural areas. However, the average concentrations in streams and wells seldom exceeded established standards and guidelines to protect human health. The highest detection frequency of pesticides occurred in shallow groundwater below agricultural and urban areas while the lowest frequency occurred in deep aquifers.

Figure 1.7 shows the distribution of pesticides in streams and groundwater associated with agricultural and urban land use. Herbicides were the most common pesticide type found in streams and groundwater in agricultural areas. Atrazine and its breakdown product, deethylatrazine, metolachlor, cyanazine, alachlor, and EPTC were the most commonly detected herbicides. They rank in the top 10 in national usage and are widely used in crop production. Atrazine was found in about two-thirds of all samples from streams. In urban streams and groundwater, insecticides were most frequently observed. Diazinon, carbaryl, chlorpyrifos, and malathion, which rank 1, 8, 4, and 13 among insecticides used for homes and gardens, were most frequently detected in streams. Atrazine, metolachlor, simazine, prometon, 2,4-D, diuron, and tebuthiuron were the most commonly detected herbicides in urban streams. These are used on lawns, gardens, and commercial areas, and in roadside maintenance.

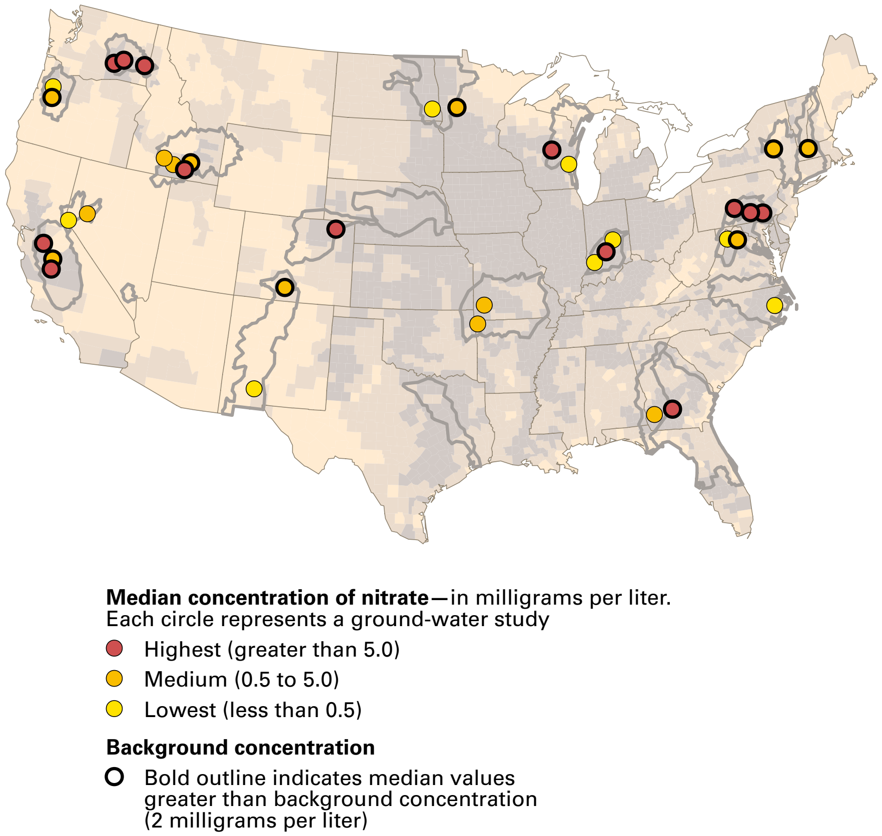


FIGURE 1.6. *Levels of nitrate in shallow groundwater. From U.S. Geological Survey, Circular 1225, 1999.*

Acid Deposition

Much concern about the effects of acid rain on plants, bodies of water, and soils has also been expressed. Acid rain also can cause damage to buildings and monuments, particularly those constructed of limestone and marble, and it can cause corrosion of certain metals.

Acid rain results from the burning of fossil fuels such as coal, which generates sulfur dioxide and nitrogen oxides, and from exhausts of motor vehicles, a main source of nitrogen oxides. These combine in the atmosphere with water and other materials to produce nitric and sulfuric acids that are often carried for long distances by wind and then fall to the earth via precipitation such as rain, snow, sleet, mist, or fog. Acidic deposition has been linked to a number of environmental issues (Table 1.2).

From 1980 to 1991 the U.S. Geological Survey monitored rainwater collected at 33 sites around the United States. Concentrations of sulfates declined greatly at 26 of the 33 sites; however, nitrates were significantly decreased at only 3 of the 33 sites. The decreases in sulfate are directly related

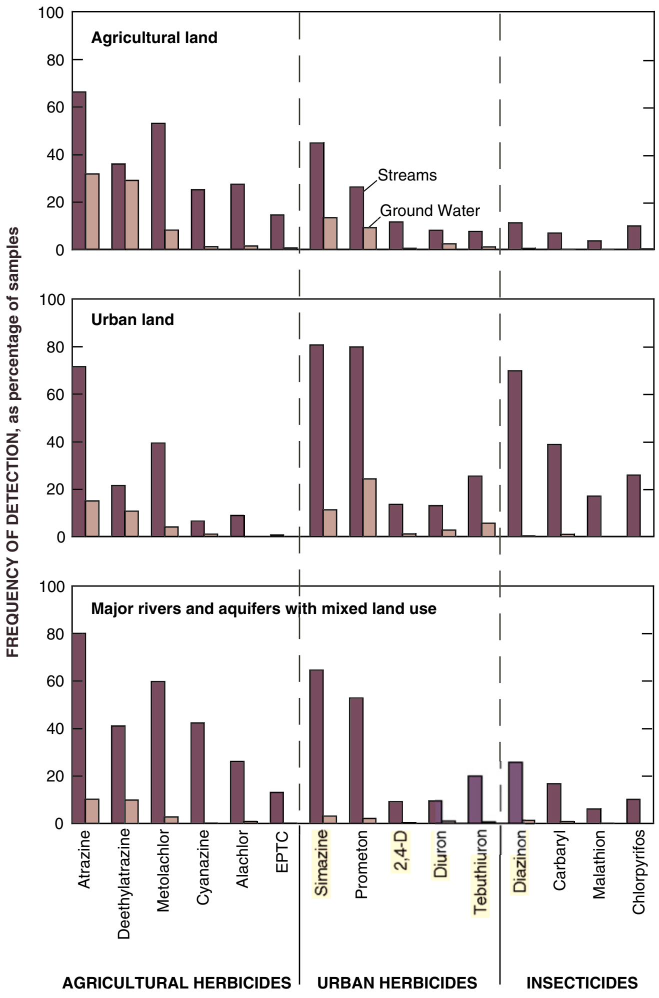


FIGURE 1.7.

Frequently detected pesticides in water of agricultural and urban areas. From U.S. Geological Survey, Circular 1225, 1999.

TABLE 1.2. *Linkages between Emissions of SO_2 and NO_x and Important Environmental Issues*[a]

Problem	Linkage to acidic deposition	Reference
Coastal eutrophication	Atmospheric deposition is important in the supply of N to coastal waters.	Jaworski *et al.* (1997)
Mercury accumulation	Surface water acidification enhances mercury accumulation in fish.	Driscoll *et al.* (1994)
Decreased visibility	Sulfate aerosols are an important component of atmospheric particulates; they decrease visibility.	Malm *et al.* (1994)
Climate change	Sulfate aerosols increase atmospheric albedo, cooling the Earth and offsetting some of the warming potential of greenhouse gases; tropospheric O_3 and N_2O act as greenhouse gases.	Moore *et al.* (1997)
Tropospheric ozone	Emissions of NO_x contribute to the formation of ozone.	Seinfeld (1986)

[a] From Driscoll *et al.* (2001).

to the 30% decrease in sulfur dioxide emissions nationwide. The less dramatic decrease in nitrate concentrations may be due to emissions from more automobiles and new power plants and factories (*New York Times*, 1993). A 10-year $500 million study funded by the U.S. Government concluded that while there is some environmental damage from acid rain, the damage is much less than originally expected. In the United States, fewer than 1200 lakes have been extensively acidified, which is about 4% of the total number of lakes in the areas where acidification might be expected. However, in certain areas, such as the Adirondack Mountains, 41% of the lakes showed chronic or episodic acidification due to acidic deposition. The acidification of surface waters can result in decreases in survival, size, and density of aquatic life such as fish (Driscoll *et al.,* 2001). Except for red spruce at high elevations, little evidence was found that acid rain caused severe damage to forests in the United States. However, over time trees could suffer nutritionally because of depletion of nutrients leached from soils. Dramatic effects of acid rain have been observed in forests in Eastern Europe where sulfur and nitrogen oxide production is not being adequately controlled. More discussion on acid rain effects on soils is provided in Chapter 9.

Trace Elements

A trace element is an element present at a level $<0.1\%$ in natural materials such as the lithosphere; if the concentrations are high enough, they can be toxic to living organisms (Adriano, 1986). Trace elements include trace metals, heavy metals, metalloids (an element having both metallic and nonmetallic properties, e.g., As and B), micronutrients (chemical elements needed in small quantities for plant growth, i.e., <50 mg g^{-1} in the plant), and trace inorganics. Heavy metals are those elements having densities greater than 5.0 g cm^{-3}. Examples are Cd, Cr, Co, Cu, Pb, Hg, and Ni. Table 1.3 shows the occurrence and significance of trace elements in natural waters.

The sources of trace elements are soil parent materials (rocks), commercial fertilizers, liming materials, biosolids, irrigation waters, coal combustion residues, metal-smelting industries, auto emissions, and others. Table 1.4 shows the concentrations of trace elements in soil-forming rocks and other natural materials, while Table 1.5 illustrates trace element concentrations in biosolids from several countries.

One metalloid of increasing concern in the environment is arsenic (As). Arsenic is a known human carcinogen. Drinking water contaminated with As has been linked to cancer, diabetes, and cardiovascular problems. The source of the As in drinking water, particularly inorganic As, is often weathering of minerals in rocks and soils.

Total As in soils ranges from 0.1 to 97 ppm with a mean concentration of 7 ppm for surface soils in the United States (Dragun, 1991). Arsenic occurs in two major oxidation states, As(III) and As(V). As(III) is primarily present in anoxic environments while As(V) is found in oxic soils. Both As species primarily occur as oxyanions in the natural environment and strongly complex

TABLE 1.3. *Occurrence and Significance of Trace Elements in Natural Waters*[a]

Element	Sources	Effects and significance	U.S. Public Health Service limit (mg $liter^{-1}$)[b]	Occurrence: % of samples, highest and mean concentrations (μg $liter^{-1}$)[c]
Arsenic	Mining by-product, pesticides, chemical waste	Toxic, possibly carcinogenic	0.05	5.5% (above 5 μg $liter^{-1}$), 336, 64
Beryllium	Coal, nuclear power, and space industries	Acute and chronic toxicity, carcinogenic	Not given	Not given
Boron	Coal, detergent formulations, industrial wastes	Toxic to some plants	1.0	98% (above 1 μg $liter^{-1}$), 5000, 101
Cadmium	Industrial discharge, mining waste, metal plating, water pipes	Replaces zinc biochemically, causes high blood pressure and kidney damage, destroys testicular tissue and red blood cells, toxic to aquatic biota	0.01	2.5%, not given, 9.5
Chromium	Metal plating, cooling-tower water additive (chromate), normally found as Cr(VI) in polluted water	Essential trace element (glucose tolerance factor), possibly carcinogenic as Cr(VI)	0.05	24.5%, 112, 9.7
Copper	Metal plating, industrial and domestic wastes, mining, mineral leaching	Essential trace element, not very toxic to animals, toxic to plants and algae at moderate levels	1.0	74.4%, 280, 15
Fluorine (fluoride ion)	Natural geological sources, industrial waste, water additive	Prevents tooth decay at above 1 mg $liter^{-1}$, causes mottled teeth and bone damage at around 5 mg $liter^{-1}$ in water	0.8–1.7 depending on temperature	Not given
Iodine (iodide)	Industrial waste, natural brines, seawater intrusion	Prevents goiter	Not given	Rare in fresh water
Iron	Corroded metal, industrial wastes, acid mine drainage, low pE water in contact with iron minerals	Essential nutrient (component of hemoglobin), not very toxic, damages materials (bathroom fixtures and clothing)	0.05	75.6%, 4600, 52

TABLE 1.3. *Occurrence and Significance of Trace Elements in Natural Waters*[a] *(contd)*

Element	Sources	Effects and significance	U.S. Public Health Service limit (mg liter^{-1})[b]	Occurrence: % of samples, highest and mean concentrations (μg liter^{-1})[c]
Lead	Industry, mining, plumbing, coal, gasoline	Toxicity (anemia, kidney disease, nervous system), wildlife destruction	0.05	19.3% (above 2 μg liter^{-1}), 140, 23
Manganese	Mining, industrial waste, acid mine drainage, microbial action on manganese minerals at low pE	Relatively nontoxic to animals, toxic to plants at higher levels, stains materials (bathroom fixtures and clothing)	0.05	51.4% (above 0.3 μg liter^{-1}), 3230, 58
Mercury	Industrial waste, mining, pesticides, coal	Acute and chronic toxicity	Not given	Not given
Molybdenum	Industrial waste, natural sources, cooling-tower water additive	Possibly toxic to animals, essential for plants	Not given	32.7 (above 2 μg liter^{-1}), 5400, 120
Selenium	Natural geological sources, sulfur, coal	Essential at low levels, toxic at higher levels, causes “alkali disease” and “blind staggers” in cattle, possibly carcinogenic	0.01	Not given
Silver	Natural geological sources, mining, electroplating, film-processing wastes, disinfection of water	Causes blue-gray discoloration of skin, mucous membranes, eyes	0.05	6.6% (above 0.1 μg liter^{-1}), 38, 2.6
Zinc	Industrial waste, metal plating, plumbing	Essential element in many metalloenzymes, aids wound healing, toxic to plants at higher levels; major component of sewage sludge, limits land disposal of sludge	5.0	76.5% (above 2 μg liter^{-1}), 1180, 64

[a] Reprinted with permission from S. E. Manahan (1991), “Environmental Chemistry.” Copyright Lewis Publishers, an imprint of CRC Press, Boca Raton, FL.

[b] U.S. Public Health Service (1962).

[c] Kopp and Kroner, “Trace Metals in Waters of the United States,” U.S. EPA. The first figure is the percentage of samples showing the element; the second is the highest value found; the third is the mean value in positive samples (samples showing the presence of the metal at detectable levels).

TABLE 1.4. *Concentrations (mg kg^{-1}) of Trace Elements in Various Soil-Forming Rocks and Other Natural Materials*[a,b]

Element	Ultramafic igneous	Basaltic igneous	Granitic igneous	Shales and clays	Black shales	Deep-sea clays	Lime-stones	Sand-stones
Arsenic	0.3–16	0.2–10	0.2–13.8	—	—	—	0.1–8.1	0.6–9.7
	3.0	2.0	2.0	10		13	1.7	2
Barium	0.2–40	20–400	300–1800	460–1700	70–1000	—	10	—
	1	300	700	700	300	2300	—	20
Beryllium	—	1.0	2–3	3	—	2.6	—	—
Cadmium	0–0.2	0.006–0.6	0.003–0.18	0–11	<0.3–8.4	0.1–1		
	0.05	0.2	0.15	1.4	1.0	0.5	0.05	0.05
Chromium	1000–3400	40–600	2–90	30–590	26–1000	—	—	—
	1800	200	20	120	100	90	10	35
Cobalt	90–270	24–90	1–15	5–25	7–100	—	—	—
	150	50	5	20	10	74	0.1	0.3
Copper	2–100	30–160	4–30	18–120	20–200	—	—	—
	15	90	15	50	70	250	4	2
Fluorine	—	20–1060	20–2700	10–7600	—	—	0–1200	10–880
		360	870	800		1300	220	180
Iron	94,000	86,500	14,000–30,000	47,200	20,000	65,000	3800	9800
Lead	—	2–18	6–30	16–150	7–150	—	—	<1–31
	1	6	18	20	30	80	9	12
Mercury	0.004–0.5	0.002–0.5	0.005–0.4	0.005–0.51	0.03–2.8	0.02–2.0	0.01–0.22	0.001–0.3
	0.1?	0.05	0.06	0.09	0.5	0.4	0.04	0.05
Molybdenum	—	0.9–7	1–6	—	1–300	—	—	—
	0.3	1.5	1.4	2.5	10	27	0.4	0.2
Nickel	270–3600	45–410	2–20	20–250	10–500	—	—	—
	2000	140	8	68	50	225	20	2
Selenium	0.05	0.05	0.05	0.6	—	0.17	0.08	0.05
Vanadium	17–300	50–360	9–90	30–200	50–1000	—	—	—
	40	250	60	130	150	120	20	20
Zinc	—	48–240	5–140	18–180	34–1500	—	—	2–41
	40	110	40	90	100?	165	20	16

[a] From Tourtelot (1971).

[b] The upper values are the usually reported range, the lower values the average.

with metal oxides such as Al and Fe oxides as inner-sphere products. These oxides, and particularly Mn oxides, can effect the oxidation of As(III) to As(V) which reduces the toxicity of As. As can also occur as sulfide minerals such as arsenopyrite (FeAsS) and enargite (Cu_3AsS_4) at mining sites.

There has been much controversy over the MCL of As in drinking water. The current standard of 50 ppb in the United States was established in 1942 by the U.S. Public Health Service. The World Health Organization recommends a 10-ppb guideline. Since 1975, the U.S. EPA has been reassessing the 50-ppb level. In 1999, the National Research Council (NRC) published a report recommending that the 50-ppb level be lowered. In 2001 the NRC issued a new report estimating that humans who consume water with 3 ppb As daily (based on 1 liter consumption day^{-1}) have a 1 in 1000 risk of developing bladder or lung cancer during their lifetime. If the level of As in drinking water is 10 ppb, the risk is more than 3 in 1000 and at 20 ppb the risk is 7 in 1000 (NRC, 2001).

The U.S. Government has agreed to lower the MCL for As to 10 ppb. This new standard will affect 13 million people, primarily in the Western United States but also in parts of the Midwest and New England where As levels in well water exceed 10 ppb (Fig. 1.8). The 10-ppb standard will cost $181 million annually.

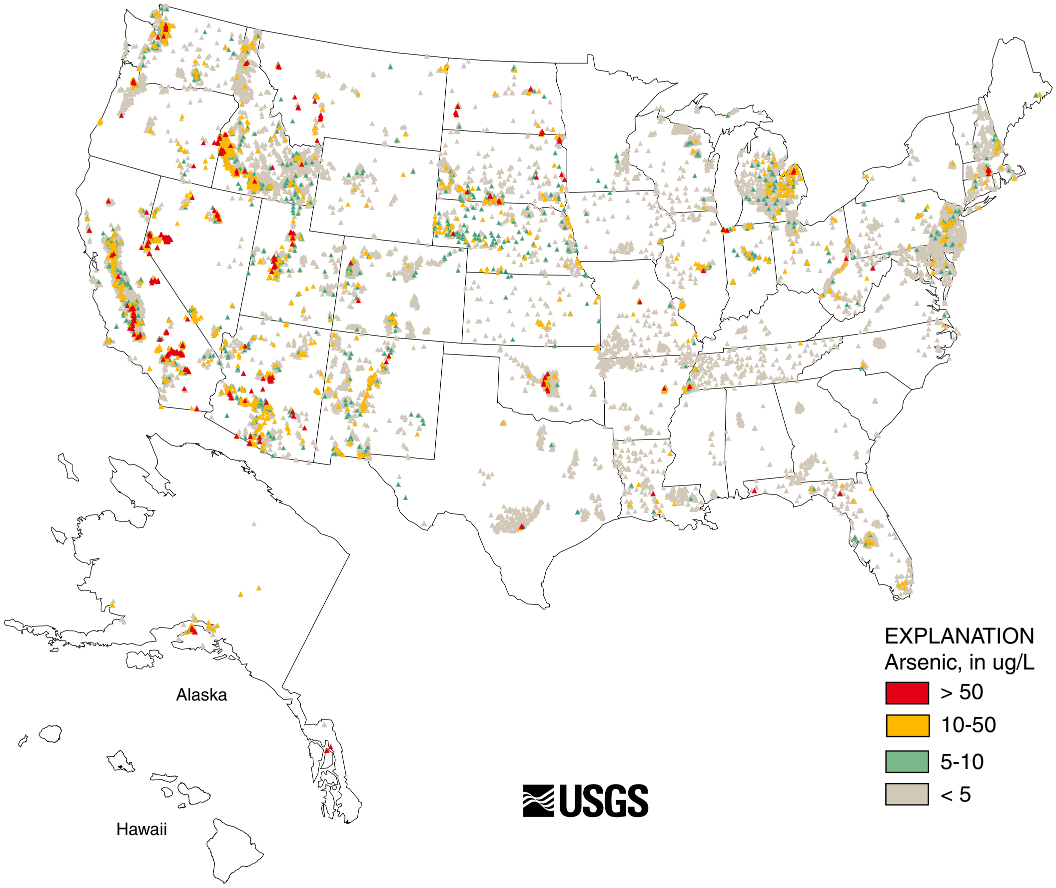


FIGURE 1.8. *Arsenic concentrations in groundwater of the United States. From Welch et al. (2000), Arsenic in groundwater resources of the United States: U.S. Geological Survey Fact Sheet 063-00.*

TABLE 1.5. *Concentrations (mg kg^{-1}) of Trace Elements in Biosolids*[a]

Element	United States[b]		United Kingdom[c]		Sweden[d]		Canada[e] (mean)	New Zealand[f] (mean)
	Mean	Range	Mean	Range	Mean	Range		
Ag	—	—	32	5–150	—	—	—	—
As	14.3	3–30	—	—	—	—	—	—
B	37.0	22–90	70	15–1,000	—	—	1,950	480
Ba	621	272–1,066	1,700	150–4,000	—	—	—	580
Be	<8.5	—	5	1–30	—	—	—	—
Bi	16.8	<1–56	34	<12–100	—	—	—	—
Cd	104	7–444	<200	<60–1,500	13	2–171	38	4.5
Co	9.6	4–18	24	2–260	15	2–113	19	21
Cr	1,441	169–14,000	980	40–8,800	872	20–40,615	1,960	850
Cu	1,346	458–2,890	970	200–8,000	791	52–3,300	1,600	720
F	167	370–739	—	—	—	—	—	—
Hg	8.6	3–18	—	—	6.0	<0.1–55	—	—
Mn	194	32–527	500	150–2,500	517	73–3,861	2,660	610
Mo	14.3	1–40	7	2–30	—	—	13	8
Ni	235	36–562	510	20–5,300	121	16–2,120	380	350
Pb	1,832	136–7,627	820	120–3,000	281	52–2,914	1,700	610
Sb	10.6	2–44	—	—	—	—	—	—
Se	3.1	1–5	—	—	—	—	—	—
Sn	216	111–492	160	40–700	—	—	—	80
Ti	2,331	1,080–4,580	2,000	<1,000–4,500	—	—	—	4,700
V	40.6	15–92	75	20–400	—	—	15	80
W	20.2	1–100	—	—	—	—	—	—
Zn	2,132	560–6,890	4,100	700–49,000	2,055	705–14,700	6,140	700

[a] From Adriano (1986), with permission from Springer-Verlag.

[b] Furr *et al.* (1976); includes Atlanta, Chicago, Denver, Houston, Los Angeles, Miami, Milwaukee, Philadelphia, San Francisco, Seattle, Washington, DC, and five cities in New York, with permission.

[c] Berrow and Webber (1972); includes 42 samples from different locations in England and Wales, with permission.

[d] Berggren and Oden (1972); from 93 treatment plants, with permission.

[e] Oliver and Cosgrove (1975); from 10 sites in southern Ontario, Canada, with permission.

[f] Wells and Whitton (1977), with permission.

Hazardous Wastes

The disposal of hazardous wastes and their effects on the environment and human health are topics of worldwide importance. There is an array of potentially hazardous waste materials. These include mining waste, acid mine drainage, wastes from metal smelting and refining industries, pulp and paper industry wastes, petroleum refining wastes, wastes from paint and allied industries, pesticide applications, inorganic fertilizers, and municipal solid waste (Yong *et al.,* 1992).

According to the Resource Conservation and Recovery Act (RCRA) of 1976, solid waste is "any garbage, refuse, sludge, from waste treatment plants, water supply treatment plants or air pollution control facilities and other discarded material including solid, liquid semisolid, or contained gaseous materials resulting from industrial, commercial, mining and agricultural activities, and from community activities, but does not include solid or dissolved material in domestic sewage or irrigation return flows." This definition includes nearly all kinds of industrial and consumer waste discharge—solid, semiliquid, and liquid.

Hazardous waste is defined as "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may: (a) cause, or significantly contribute to an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed" (Resource Conservation and Recovery Act, 1976, Public Law 94-580).

Case Study of Pollution of Soils and Waters

An extensive case study that illustrates pollution of Department of Energy (DOE) sites and military bases in the United States has recently been conducted (Table 1.6). These are located around the United States and were sites for weapons production. Substantial radioactive wastes were produced. At some military bases toxic chemicals were disposed of in water supplies and other areas that are now leaking.

A report (Riley *et al.,* 1992) documented contamination of soils/sediments and groundwater at 91 waste sites on 18 DOE facilities. These facilities occupy 7280 km^2 in the 48 contiguous states. Most of the wastes were disposed of on the ground or in ponds, pits, injection wells, and landfills, and are contaminating the subsurface environment. Contamination is also resulting from leaking underground storage tanks and buried chemicals and wastes. The results of the survey found 100 individual chemicals or mixtures in the groundwater and soil/sediments of these sites.

TABLE 1.6. *Contamination at U.S. Energy Department Sites and Costs of Cleanup*[a]

Site and location	Type of contamination	Spent as of Sept. 1990 on cleanup[b]	Estimated or approved cost of cleanup[b]
1. Hanford Nuclear Reservation[c] (Richland, WA)	Plutonium and other radioactive nuclides, toxic chemicals, heavy metals, leaking radioactive-waste tanks, groundwater and soil contamination, seepage into the Columbia River	$1,000 plus	$30,000–50,000
2. McClellan Air Force Base[d] (Sacramento, CA)	Solvents, metal-plating wastes, degreasers, paints, lubricants, acids, PCBs in groundwater	61.0	170.5
3. Hunters Point Naval Air Station[e] (San Francisco, CA)	Chemical spills in soil, heavy metals, solvents	21.5	114.0
4. Lawrence Livermore National Laboratory[c] (Livermore, CA)	Chemical and radioactive contamination of buildings and soils	N.A.	1,000 plus
5. Castle Air Force Base[d] (Merced, CA)	Solvents, fuels, oils, pesticides, cyanide, cadmium in soil, landfills, and disposal pits	12.7	90.0
6. Edwards Air Force Base[e] (Kern County, CA)	Oil, solvents, petroleum by-products in abandoned sites and drum storage area	21.0	53.4
7. Nevada Test Site[c] (near Las Vegas, NV)	Radioactive groundwater contamination	100 plus	1,000 plus
8. Idaho National Engineering Laboratory[c] (near Idaho Falls, ID)	Radioactive wastes, contamination of Snake River aquifer, chemical-waste lagoons	N.A.	5,000 plus
9. Tooele Army Depot[f] (Tooele County, UT)	Heavy metals, lubricants, paint primers, PCBs, plating and explosives wastes in groundwater and ponds	10.0	64.4
10. Rocky Mountain Arsenal[f] (Denver, CO)	Pesticides, nerve gas, toxic solvents, and fuel oil in shallow, leaking pits	315.5	2,037.1
11. Rocky Flats Plant[c] (Golden, CO)	Plutonium, americium, chemicals, other radioactive wastes in groundwater, lagoons and dump sites	200 plus	1,000 plus
12. Los Alamos National Laboratory[c] (Los Alamos, NM)	Millions of gallons of radioactive and toxic chemical wastes poured into ravines and canyons across hundreds of sites	N.A.	1,000 plus
13. Tinker Air Force Base[d] (Oklahoma City, OK)	Trichloroethylene and chromium in underground water	20.1	69.7
14. Twin Cities Army Ammunition Plant[f] (New Brighton, MN)	Chemical by-products and solvents from ammunition manufacturing	28.0	59.9
15. Lake City Army Ammunition Plant[f] (Independence, MO)	Toxic metals and chemicals in groundwater	25.9	55.1

TABLE 1.6. *Contamination at U.S. Energy Department Sites and Costs of Cleanup*[a] *(contd)*

Site and location	Type of contamination	Spent as of Sept. 1990 on cleanup[b]	Estimated or approved cost of cleanup[b]
16. Louisiana Army Ammunition Plant[f] (Doyline, LA)	Hazardous wastes, groundwater contamination	38.0	66.9
17. Oak Ridge National Laboratory[c] (Oak Ridge, TN)	Mercury, radioactive sediments in streams, lakes, and groundwater	1,000 plus	4,000–8,000
18. Griffiss Air Force Base[d] (Rome, NY)	Heavy metals, greases, solvents, caustic cleaners, dyes in tank farms and groundwater and disposal sites	7.3	100.0
19. Letterkenny Army Depot[f] (Franklin County, PA)	Oil, pesticides, solvents, metal-plating wastes, phenolics, painting wastes in soil and water	11.9	56.2
20. Naval Weapons Station[e] (Colts Neck, NJ)	Heavy metals, lubricants, oil, corrosive acids in pits and disposal sites	1.1	33.8
21. Aberdeen Proving Ground[f] (Aberdeen, MD)	Arsenic, napalm, nitrates, and chemical warfare agents contaminating soil and groundwater	19.8	579.4
22. Camp Lejeune Military Reservation[e] (Jacksonville, NC)	Lithium batteries, paints, thinners, pesticides, PCBs in soil and potentially draining into New River	3.0	59.0
23. Cherry Point Marine Air Corps Station[e] (Cherry Point, NC)	Untreated wastes soaking creek sediments with heavy metals, industrial wastes, and electroplating wastes	1.6	51.6
24. Savannah River Site[c] (Aiken, SC)	Radioactive waste burial grounds, toxic chemical pollution, contamination of groundwater	N.A.	5,000 plus
25. Mound Laboratory[c] (Miamisburg, OH)	Plutonium in soil and toxic chemical wastes	150 plus	500 plus
26. Feed Materials Production Center[c] (Fernald, OH)	Uranium and chemicals in ponds and soil	600 plus	1,000–3,000

[a] From Energy Department, Air Force, Army, Navy, General Accounting Office; *New York Times*, August 15, 1991.

[b] Army, Navy, and Air Force figures represent costs for committed or approved cleanup activities. Energy Department figures represent total estimated costs. All costs are in millions of dollars.

[c] Energy Department site.

[d] Air Force site.

[e] Navy site.

[f] Army site.

The most prevalent metals were Pb, Cr, As, and Zn while the major anion found was NO_3^- (Fig. 1.9). Greater than 50% of all DOE facilities contained 9 of the 12 metals and anions shown in Fig. 1.9 in the groundwater. The sources of the metals and anions are associated with reactor operations (Cr and Pb), irradiated fuel processing (NO_3^-, Cr, CN^-, and F^-), uranium recovery (NO_3^-), fuel fabrication (Cr, NO_3^-, and Cu), fuel production (Hg), and isotope separation (Hg) (Stenner *et al.,* 1988; Rogers *et al.,* 1989; Evans *et al.,* 1990). The most prevalent inorganic species in soils/sediments at the DOE sites were Cu, Cr, Zn, Hg, As, Cd, and NO_3^- (Fig. 1.9). Radionuclides that were most common in groundwater were tritium, U, and Sr. In soils/sediments, U, Pu, and Cs were the most prevalent.

Figure 1.10 shows that 19 chlorinated hydrocarbons were found in the groundwaters. The most common ones were trichloroethylene, 1,1,1-trichloroethane and 1,2-dichloroethylene, tetrachloroethylene, 1,1-dichloroethane, and chloroform. In soils/sediments, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, and dichloromethane were found at 50% or more of the sites. Fuel hydrocarbons most often found in groundwaters were toluene, xylene, benzene, and ethylbenzene. In soils/sediments the same fuel hydrocarbons were most often found but some polyaromatic hydrocarbons, such as phenanthrene, anthracene, and fluoranthene, also were detected. These latter compounds are not very soluble, which explains why they were not detected in the groundwaters. Sources of the high-molecular-weight hydrocarbons were coal and coal wastes (fly ash) from coal-fired electric power and steam-generating facilities located at many of the DOE sites. Sources of low-

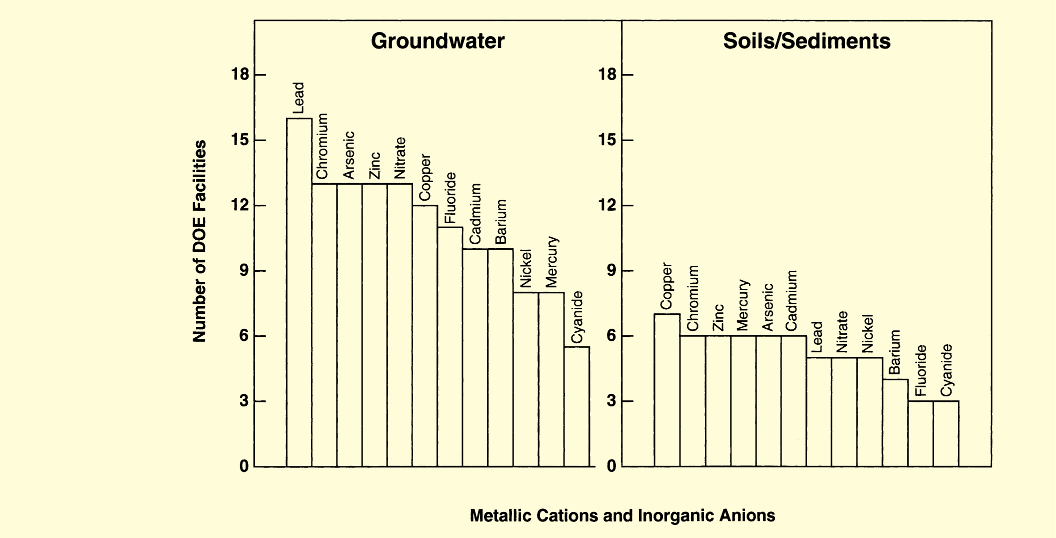


FIGURE 1.9. *Frequency of occurrence of selected metals and inorganic anions in groundwater and soils/sediments at DOE facilities. From Riley et al. (1992), with permission. This research or report was supported by the Subsurface Science program, Office of Health and Environmental Research, U.S. Department of Energy (DOE).*

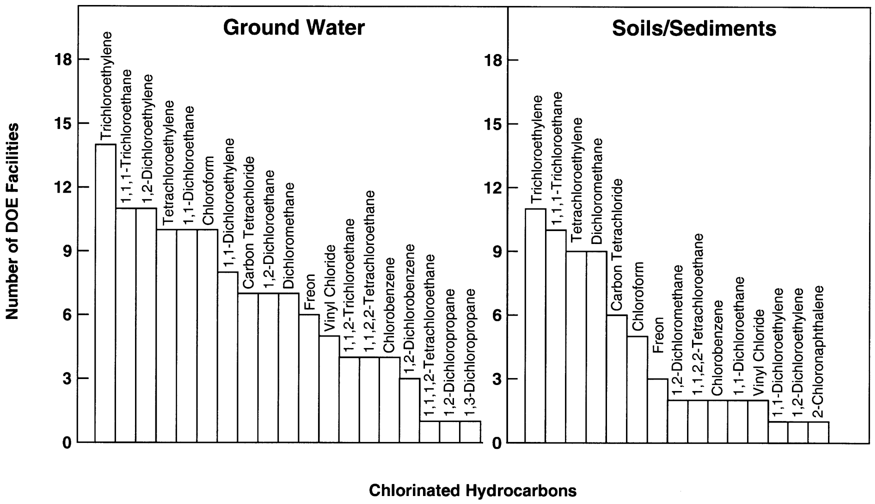


FIGURE 1.10. *Frequency of occurrence of chlorinated hydrocarbons in groundwater and soils/sediments at DOE facilities. From Riley et al. (1992), with permission. This research or report was supported by the Subsurface Science program, Office of Health and Environmental Research, U.S. Department of Energy (DOE).*

molecular-weight hydrocarbons were gasoline- and petroleum-derived fuels from leaking above- and underground tanks. Ketones, primarily acetone, methyl ethyl ketone, and methyl isobutyl ketone, were found in the groundwater, while acetone was the most prevalent ketone found in soils/sediments. Ketones are employed in nuclear fuels processing.

Other chemicals and compounds detected less frequently at the DOE sites included phthalates, pesticides, and chelating agents (e.g., EDTA, ethylenediaminetetraacetic acid), and organic acids such as oxalic and citric acids.

Soil Decontamination

Numerous attempts to decontaminate polluted soils with the use of an array of both *in situ* and non-*in-situ* techniques are being made (Table 1.7). None of these is a panacea for remediating contaminated soils and often more than one of the techniques may be necessary to optimize the cleanup effort. The complexity of soils and the presence of multiple contaminants also makes most remediation efforts arduous and costly (Sparks, 1993).

In Situ Methods

In situ methods are used at the contamination site. Soil does not need to be excavated, and therefore exposure pathways are minimized.

TABLE 1.7. *In situ and Non-in-Situ Techniques Used in Soil Decontamination*[a]

Technology	Advantages	Limitations	Relative costs
In situ			
Volatilization	Can remove some compounds resistant to biodegradation	Volatile organic compounds only	Low
Biodegradation	Effective on some nonvolatile compounds	Long-term timeframe	Moderate
Phytoremediation	Effective with a number of inorganic and organic chemicals	Plants are often specific for particular contaminants	Low to medium
Leaching	Could be applicable to wide variety of compounds	Not commonly practiced	Moderate
Vitrification		Developing technology	High
Passive	Lowest cost and simplest to implement	Varying degrees of removal	Low
Isolation/containment	Physically prevents or impedes migration	Compounds not destroyed	Low to moderate
Non-*in-situ*			
Land treatment	Uses natural degradation processes	Some residuals remain	Moderate
Thermal treatment	Complete destruction possible	Usually requires special features	High
Asphalt incorporation	Use of existing facilities	Incomplete removal of heavier compounds	Moderate
Solidification	Immobilizes compounds	Not commonly practiced for soils	Moderate
Groundwater extraction and treatment	Product recovery, groundwater restoration		Moderate
Chemical extraction		Not commonly practiced	High
Excavation	Removal of soils from site	Long-term liability	Moderate

[a] Adapted from Preslo *et al.* (1988). Copyright Lewis Publishers, an imprint of CRC Press, Boca Raton, FL.

VOLATILIZATION

In situ volatilization causes mechanical drawing or air venting through the soil. A draft fan is injected or induced, which causes an air flow through the soil, via a slotted or screened pipe, so that air can flow but entrainment of soil particles is restricted. Some treatment, e.g., activated carbon, is used to recover the volatilized contaminant. This technique is limited to volatile organic carbon materials (Sparks, 1993).

BIODEGRADATION

In situ biodegradation involves the enhancement of naturally occurring microorganisms by stimulating their numbers and activity. The microorganisms then assist in degrading the soil contaminants. A number of soil, environmental, chemical, and management factors affect biodegradation of soil pollutants including moisture content, pH, temperature, the microbial community present, and the availability of nutrients. Biodegradation is facilitated by aerobic soil conditions and soil pH in the range of 5.5–8.0, with an optimal pH of about 7 and temperature in the range of 293–313 K. It is important to realize that a microbe may be effective in degrading one pollutant, but not another. Moreover, microbes may be effective in degrading one form of a specific pollutant but not another.

PHYTOREMEDIATION

The use of plants to decontaminate soils and water (phytoremediation) can be quite effective (Fig. 1.11). There are hundreds of plant species that can detoxify pollutants. For example, sunflowers can absorb uranium, certain ferns have high affinity for As, alpine herbs absorb Zn, mustards can absorb Pb, clovers take up oil, and poplar trees destroy dry-cleaning solvents (*New York Times*, 2001).

Recently the brake fern *(Pteris vittata)* was found to be an As hyperaccumulator (Brooks, 1998) and very effective in remediation of a Central Florida soil contaminated with chromated copper arsenate (Ma *et al.,* 2001). Brake ferns extracted 1,442–7,526 mg kg^{-1} As from the contaminated soils. The uptake of As into the fern fronds was rapid, increasing from 29.4 to 15,861 in two weeks. Almost all of the As present in the plant was inorganic, and there were indications that As(V) was converted to As(III) during translocation from roots to fronds.

LEACHING

This method involves leaching the in-place soil with water and often with a surfactant (a surface-active substance that consists of hydrophobic and hydrophilic regions; surfactants lower the surface tension) to remove the contaminants. The leachate is then collected, downstream of the site, using a collection system for treatment and/or disposal. The use of this method has been limited since large quantities of water are often used to remove the pollutants and, consequently, the waste stream is large and disposal costs can be high.

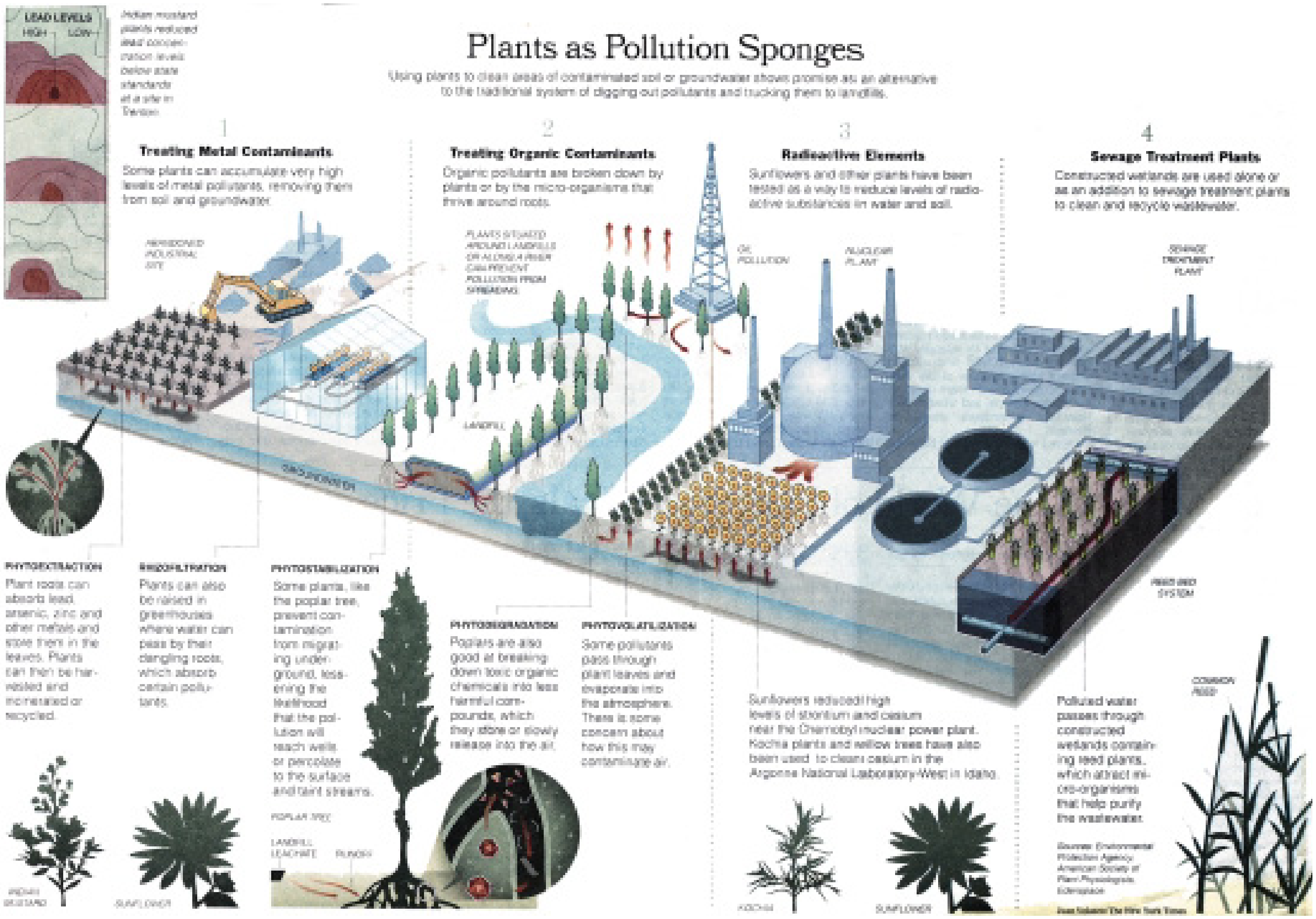
The effectiveness of a leaching technique also depends on the permeability, porosity, homogeneity, texture, and mineralogy of the soil, which all affect the desorbability (release) of the contaminant from the soil and the leaching rate of contaminants through the soil (Sparks, 1993).

VITRIFICATION

In *in situ* vitrification the contaminants are solidified with an electric current, resulting in their immobilization. Vitrification may immobilize pollutants for as long as 10,000 years. Since a large amount of electricity is necessary, the technique is costly.

ISOLATION/CONTAINMENT

With this method, contaminants are held in place by installing subsurface physical barriers such as clay liners and slurry walls to minimize lateral migration. Scientists and engineers have also added surfactants to clay minerals (organo-clays) to enhance retention of organic pollutants (Xu *et al.,* 1997) and used organo-clays in liners to minimize the mobility of pollutants and in wastewater treatment (Soundararajan *et al.,* 1990). Further discussion of organo-clays is provided in Chapter 2.



Plants as Pollution Sponges

Using plants to clean areas of contaminated soil or groundwater shows promise as an alternative to the traditional system of digging out pollutants and trucking them to landfills.

Indian mustard plants reduced lead concentration levels below state standards at a site in Trenton.

1 Treating Metal Contaminants

Some plants can accumulate very high levels of metal pollutants, removing them from soil and groundwater.

2 Treating Organic Contaminants

Organic pollutants are broken down by plants or by the micro-organisms that thrive around roots.

3 Radioactive Elements

Sunflowers and other plants have been tested as a way to reduce levels of radioactive substances in water and soil.

4 Sewage Treatment Plants

Constructed wetlands are used alone or as an addition to sewage treatment plants to clean and recycle wastewater.

Plants situated around landfills or along a river can prevent pollution from spreading.

PHYTOEXTRACTION
Plant roots can absorb lead, arsenic, zinc and other metals and store them in the leaves. Plants can then be harvested and incinerated or recycled.

RHIZOFILTRATION
Plants can also be raised in greenhouses where water can pass by their dangling roots, which absorb certain pollutants.

PHYTOSTABILIZATION
Some plants, like the poplar tree, prevent contamination from migrating underground, lessening the likelihood that the pollution will reach wells or percolate to the surface and taint streams.

PHYTODEGRADATION
Poplars are also good at breaking down toxic organic chemicals into less harmful compounds, which they store or slowly release into the air.

PHYTOVOLATILIZATION
Some pollutants pass through plant leaves and evaporate into the atmosphere. There is some concern about how this may contaminate air.

Sunflowers reduced high levels of strontium and cesium near the Chernobyl nuclear power plant. Kochia plants and willow trees have also been used to clean cesium in the Argonne National Laboratory-West in Idaho.

Polluted water passes through constructed wetlands containing reed plants, which attract micro-organisms that help purify the wastewater.

Sources: Environmental Protection Agency; American Society of Plant Physiologists; Edenspace

[illegible]/The New York Times

FIGURE 1.11. *Schematic showing multiple use of plants in environmental remediation. From New York Times (2001), with permission.*

PASSIVE REMEDIATION

With this method, natural processes such as volatilization, aeration, biodegradation, and photolysis are allowed to occur; these processes may cause decontamination. Passive remediation is simple and inexpensive and requires only monitoring of the site. Factors that affect this type of remediation include biodegradation, adsorption, volatilization, leaching, photolysis, soil permeability, groundwater depth, infiltration, and the nature of the contaminant.

Non-in-Situ Methods

Non-*in-situ* methods involve removal of the contaminated soil, usually by excavation, and the soil is then treated on-site, or transported to another location and then treated. With these methods there are obviously concerns about exposure of the contaminants in the moving and hauling process.

LAND TREATMENT

With this technique, the contaminated soil is excavated and spread over land so that natural processes such as biodegradation or photodegradation can occur to decontaminate the soil. The land area is prepared by grading to remove rocks and other debris and the area is surrounded by berms to lessen runoff. The soil pH is adjusted to 7.0 to immobilize heavy metals and to enhance the activity and effectiveness of soil microbes. Nutrients are also added for microbial stimulation. The contaminated soil is then spread on the site and mixed with the other soil to enhance the contact between the contaminant and microbes and to promote aerobic conditions (Sparks, 1993).

THERMAL TREATMENT

With thermal treatment, the excavated soil is exposed to high heats using a thermal incinerator. The high temperature breaks down the pollutants, and the released volatiles are then collected and moved through an afterburner and combusted or recovered with solvents.

ASPHALT INCORPORATION

With this method, contaminated soils are put into hot asphalt mixes. These mixtures are then used in paving. The asphalt and soil are heated while they are mixed. This causes volatilization or decomposition of some of the contaminants. The remaining pollutants are then immobilized in the asphalt.

SOLIDIFICATION/STABILIZATION

This technique involves the addition of an additive to excavated, contaminated soil so that the contaminants are encapsulated. The mixture is then landfilled. Thus, the contaminants are not free to move alone; however, they are not destroyed. This method has been employed to minimize inorganic pollutant contamination.

CHEMICAL EXTRACTION

In this treatment the excavated soil is mixed with a solvent, surfactant, or solvent/surfactant mixture to remove the contaminants. The solvent/surfactant and released contaminants are then separated from the soil. The soil is then washed or aerated to remove the solvent/surfactant and the latter is then filtered for fine particles and treated to remove the contaminants. This technique is expensive and is not often used.

EXCAVATION

With this method, the contaminated soil is removed and disposed elsewhere (e.g., a landfill). Landfills usually contain liners, such as clay, that diminish the mobility of the contaminants, or the landfills should be located on sites where the soil permeability is low. Landfills require large land areas and often pose hazards for humans. Excavation and disposal costs are high, and there are also liability problems, safety concerns, odor production, and potential runoff and groundwater contamination problems.

Molecular Environmental Soil Chemistry

It has become increasingly recognized that if we are going to predict and model fate/transport, toxicity, speciation (form of), bioavailability, and risk assessment of plant nutrients, toxic metals, oxyanions, radionuclides, and organic chemicals at the landscape scale, we must have fundamental information at multiple scales, and our research efforts must be multi- and interdisciplinary (Fig. 1.12).

With the advent of state-of-the-art analytical techniques, some of which are synchrotron-based (see discussions that follow), one can elucidate reaction mechanisms at small scale. This has been one of the major advances in the environmental sciences over the past decade. The use of small-scale techniques in environmental research has resulted in a new multidisciplinary field of study that environmental soil chemists are actively involved in—molecular environmental science. Molecular environmental science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level.

There are a number of areas in environmental soil chemistry where the application of molecular environmental science is resulting in major frontiers. These include speciation of contaminants, which is essential for understanding release mechanisms, spatial resolution, chemical transformations, toxicity, bioavailability, and ultimate impacts on human health; mechanisms of microbial transformations, e.g., bioremediation; phytoremediation; development of predictive models; effective remediation and waste management strategies; and risk assessment. The application of molecular environmental science will be illustrated throughout the following chapters.

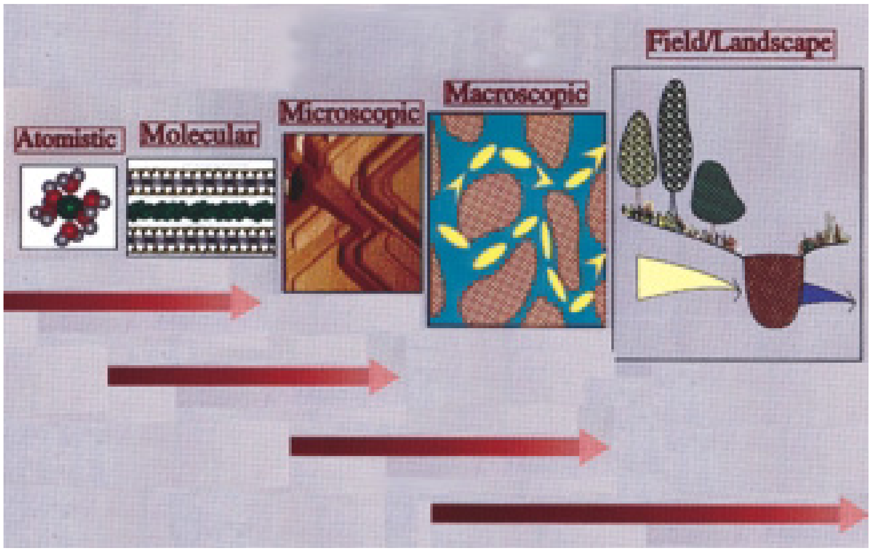


FIGURE 1.12. *Illustration of the various spatial scales that environmental scientists are interested in. From Bertsch and Hunter (1998), with permission.*

Electromagnetic Spectrum of Light

The use of intense light to understand mechanisms of soil chemical reactions and processes has revolutionized the field of environmental soil chemistry, or more appropriately, molecular environmental soil chemistry.

The electromagnetic spectrum of light is shown in Fig. 1.13. Electromagnetic radiation has both particle and wave properties such that light at a particular wavelength corresponds to a particular scale of detection (O'Day, 1999). For example, longer wave radiation detects larger objects while shorter wave radiation detects smaller objects. Light employed to see an object must have a wavelength similar to the object's size. Light has wavelengths longer or shorter than visible light. On the longer side are radio waves, microwaves, and infrared radiation. Shorter wavelength light includes ultraviolet, X-rays, and gamma rays. The shorter the wavelength, the higher the frequency and the more energetic or intense is the light. Light generated at shorter wavelengths such as X-rays is not visible by the human eye and must be detected via special means.

Each region of the spectrum is characterized by a range of wavelengths and photon energies that will determine the degree to which light will penetrate and interact with matter. At wavelengths from 10^{-7} to 10^{-10} m, one can explore the atomic structure of solids, molecules, and biological structures. Atoms, molecules, proteins, chemical bond lengths, and minimum distances between atomic planes in crystals fall within this wavelength range and can be detected. The binding energies of many electrons in atoms, molecules, and biological systems fall in the range of photon energies between 10 and

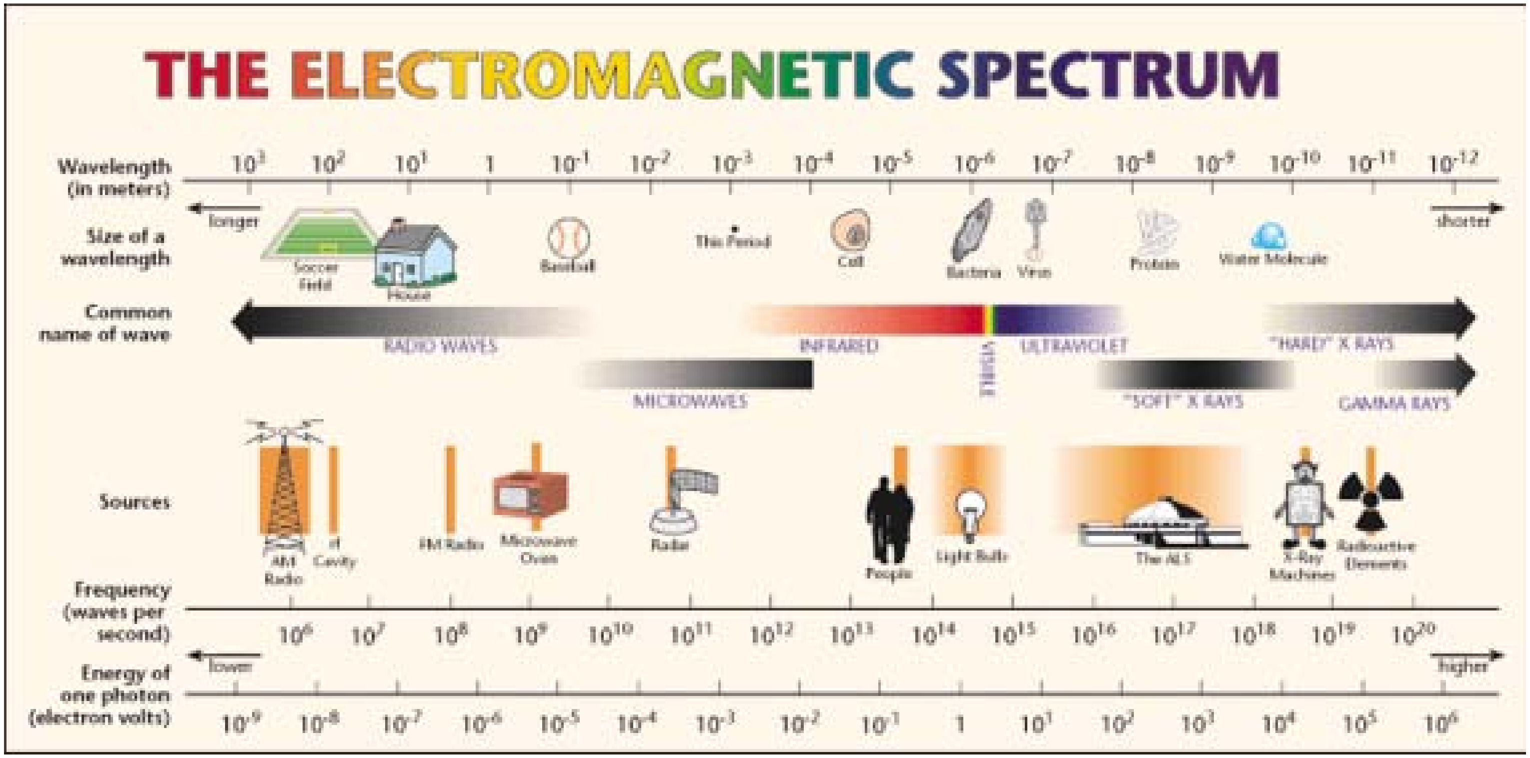


FIGURE 1.13. *Electromagnetic spectrum of light covering a wide range of wavelengths and photon energies. Courtesy of the Advanced Light Source, Lawrence Berkeley National Laboratory.*

10,000 eV. When absorbed by an atom, a photon causes an electron to separate from the atom or can cause the release or emission of other photons. By detecting and analyzing such e^- or photon emissions, scientists can better understand the properties of a sample.

Synchrotron Radiation

Intense light can be produced at a synchrotron facility. Synchrotron radiation is produced over a wide range of energies from the infrared region with energies <1 eV to the hard X-ray region with energies of 100 keV or more. There are a number of synchrotron facilities throughout the world (Table 1.8). In the United States major facilities are found at National Laboratories. These include the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, the Advanced Photon Source (APS) at Argonne National Laboratory (Fig. 1.14), the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, and the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University. The NSLS and SSRL are second- and first-generation hard X-ray light sources, respectively, the APS is a third-generation hard X-ray light source, and the ALS offers a third-generation soft X-ray source.

TABLE 1.8. *Selected First-, Second-, and Third-Generation Synchrotron Research Facilities*[a]

Acronym	Facility	Location
	First-Generation Sources	
SSRL	Stanford Synchrotron Radiation Laboratory	Stanford, CA
CHESS	Cornell High Energy Synchrotron Source	Ithaca, NY
LURE	Laboratoire pour l'Utilisation de Rayonnement Electromagnétique	Orsay, France
HASYLAB	Hamburger Synchrotronstrahlungs Labor	Hamburg, Germany
	Second-Generation Sources	
SRS	Synchrotron Radiation Source	Daresbury, United Kingdom
KEK	Photon Factory	Tsukuba, Japan
NSLS	National Synchrotron Light Source	Upton, NY
BESSY	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung	Berlin, Germany
	Third-Generation Sources	
APS	Advanced Photon Source	Argonne, IL
ALS	Advanced Light Source	Berkeley, CA
ESRF	European Synchrotron Radiation Facility	Grenoble, France
SPring-8	Super Photon ring—8 GeV	Nishi Harima, Japan

[a] See Winick and Williams (1991) for a complete list worldwide. From Schulze and Bertsch (1999), with permission.

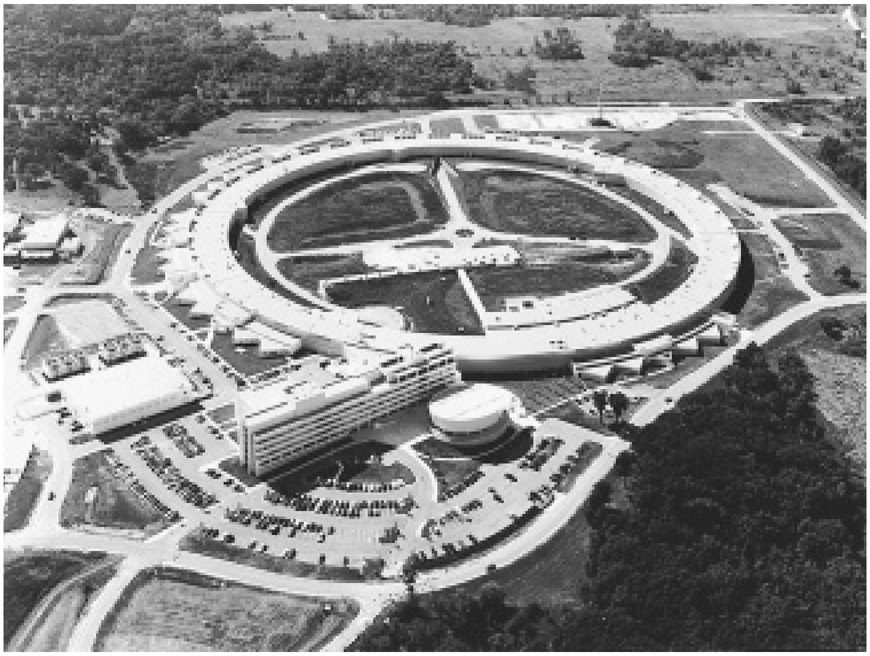


FIGURE 1.14. *The Advanced Photon Source (APS), Argonne National Laboratory. Courtesy of the Advanced Photon Source, Argonne National Laboratory.*

Synchrotrons are large machines (Fig. 1.15). The APS has a storage ring that is 1,104 m in circumference (Fig. 1.14) while the NSLS storage ring is 170 m in circumference. In the synchrotron, charged particles, either e^- or positrons, are injected into a ring-shaped vacuum chamber maintained at an ultra-high vacuum ($\sim 10^{-9}$ Torr). The particles enter the ring by way of an injection magnet and then travel around the ring at or near the speed of light, steered by bending magnets. Additional magnets focus and shape the particle beam as it travels around the ring. Synchrotron radiation or light is emitted when the charged particles go through the bending magnets, or through insertion devices, which are additional magnetic devices called wigglers or undulators inserted into straight sections of the ring. Beamlines allow the X-rays to enter experimental stations, which are shielded rooms that contain instrumentation for conducting experiments (Schultze and Bertsch, 1999).

Synchrotron radiation has enabled soil and environmental scientists to employ a number of spectroscopic and microscopic analytical techniques to understand chemical reactions and processes at molecular and smaller scales. Spectroscopies (Table 1.9) reveal chemical information and deal with the interaction of electromagnetic radiation with matter. A large number of spectroscopic techniques are a function of both large frequency or energy ranges of electromagnetic radiation involved and the approach used for probing the interaction over a given frequency range (Bertsch and Hunter, 1998). Microscopic techniques (Table 1.9) provide spatial information and arise from the interaction of energy with matter that either focuses or rasters radiation in some way to produce an image (O'Day, 1999).

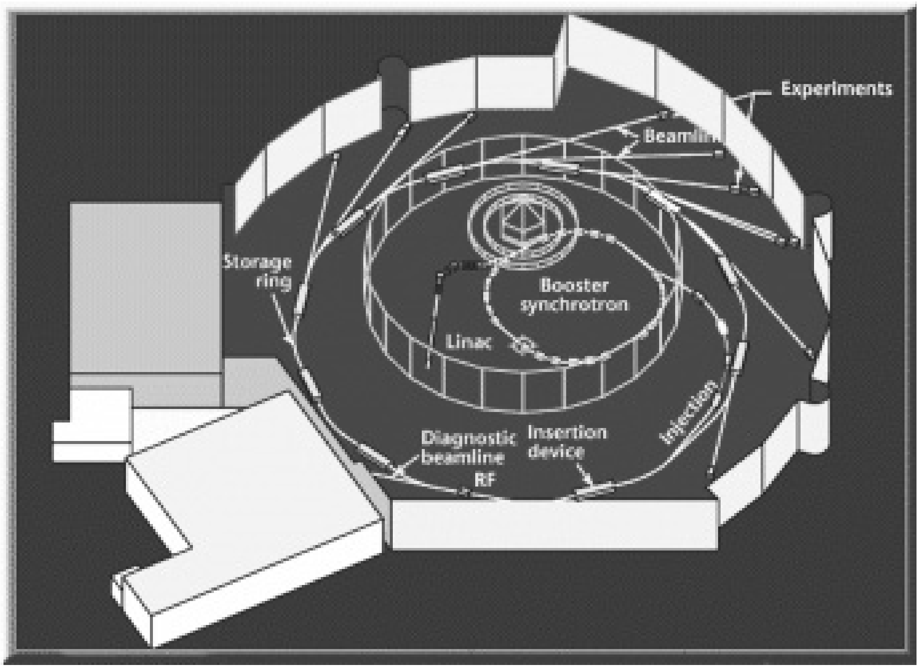


FIGURE 1.15. *Schematic diagram of a synchrotron X-ray source. Courtesy of the Advanced Light Source, Lawrence Berkeley National Laboratory.*

X-Ray Absorption Spectroscopy

One of the most widely used synchrotron-based spectroscopic techniques is X-ray absorption spectroscopy (XAS). XAS can be used to study most elements in crystalline or non-crystalline solid, liquid, or gaseous states over a concentration range of a few milligrams per liter to the pure element. It is also an *in situ* technique, which means that one can study reactions in the presence of water. This is a major advantage over many molecular scale techniques, which are *ex situ*, often requiring drying of the sample material, placing it in an ultra-high vacuum (UHV), heating the sample, or employing particle bombardment. Such conditions can alter the sample, creating artifacts, and do not simulate most natural soil conditions. XAS is an element-specific, bulk method that yields information about the local structural and compositional environment of an absorbing atom. It “sees” only the 2 or 3 closest shells of neighbors around an absorbing atom (<6 Å; note that Å will be used rather than nm to describe XAS analyses since Å is the standard unit used in the XAS scientific literature) due to the short electron mean free path in most substances. Using XAS one can ascertain important soil chemical information such as the oxidation state, information on next nearest neighbors, bond distances (accurate to ±0.02 Å), and coordination numbers (accurate to ±15–20%) (Brown *et al.,* 1995). Application of XAS to various soil chemical processes will be provided in later chapters.

TABLE 1.9. *Summary of Selected Analytical Methods for Molecular Environmental Soil Chemistry*[a]

	Type of energy	
Analytical method	**Source**	**Signal**
Absorption, emission, and relaxation spectroscopies		
IR[b] and FTIR	Infrared radiation	Transmitted infrared radiation
Synchrotron XAS (XANES and EXAFS)	Synchrotron X-rays	Transmitted or fluorescent X-rays; electron yield
Synchrotron microanalysis (XRF, XANES)	Synchrotron X-rays	Fluorescent X-rays
EELS (also called PEELS)	Electrons	Electrons
XPS and Auger spectroscopy	X-rays	Electrons
Resonance spectroscopies		
NMR	Radio waves (+ magnetic field)	Radio waves
ESR (also called EPR)	Microwaves (+ magnetic field)	Microwaves
Scattering and ablation		
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X-rays (synchrotron or laboratory)	Scattered X-rays
SIMS	Charged ion beam	Atomic mass
LA-ICP-MS	Laser	Atomic mass
Microscopies		
STM	Tunneling electrons	Electronic perturbations
AFM (also called SFM)	Electronic force	Force perturbation
HR-TEM and STEM	Electrons	Transmitted or secondary electrons
SEM/EM with EDS or WDS chemical analysis	Electrons	Secondary, or backscattered electrons; fluorescent X-rays

[a] From O'Day (1999), with permission.

[b] Abbreviations are IR, infrared; FTIR, Fourier transform infrared; XAS, X-ray absorption spectroscopy; XANES, X-ray absorption near-edge structure; EXAFS, extended X-ray absorption fine structure; XRF, X-ray fluorescence; EELS, electron energy loss spectroscopy; PEELS, parallel electron energy loss spectroscopy; XPS, X-ray photoelectron spectroscopy; NMR, nuclear magnetic resonance; ESR, electron spin resonance (also known as EPR); EPR, electron paramagnetic resonance (also known as ESR); SAXS, small-angle X-ray scattering; WAXS, wide-angle X-ray scattering; SIMS, secondary ion mass spectrometry; LA-ICP-MS, laser ablation inductively coupled plasma mass spectrometry; STM, scanning tunneling microscopy; AFM, atomic force microscopy (also known as scanning force microscopy, SFM); HR-TEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy; SEM, scanning electron microscopy; EM, electron microscopy; EDS, energy dispersive spectrometry; WDS, wavelength dispersive spectrometry.

An XAS experiment, which results in a spectrum (Fig. 1.16), consists of exposing a sample to an incident monochromatic beam of synchrotron X-rays, which is scanned over a range of energies below and above the absorption edge (K, L, M) of the element of interest. When X-rays interact with matter a number of processes can occur: X-ray scattering production of optical photons, production of photoelectrons and Auger electrons, production of fluorescence X-ray photons, and positron–electron pair production.

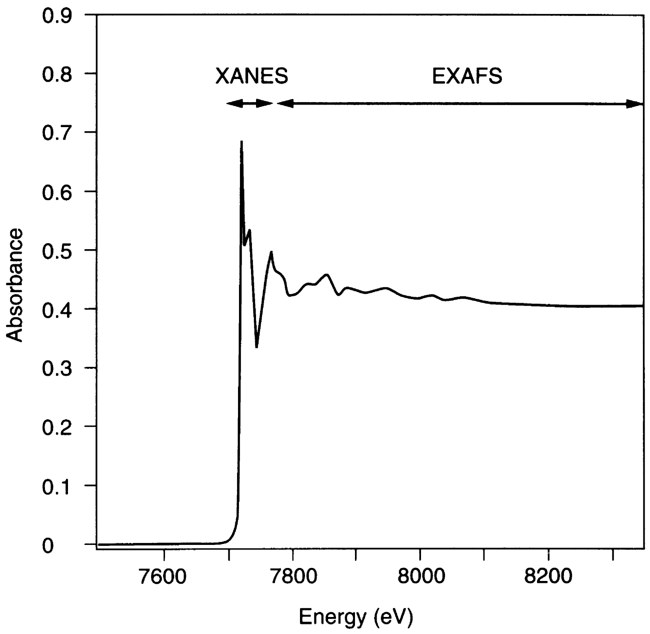


FIGURE 1.16. *Co K-edge X-ray absorption spectrum of $CoCO_3$ recorded in the transmission mode showing the XANES and EXAFS regions. The preedge region is from a few eV to ≈10 eV below the main absorption edge and shows a small preedge feature due to a 1s → 3d bound-state electron transition. From Xu (1993), with permission.*

In the X-ray energy range of 0.5 to 100 keV, photoelectron production dominates and causes X-ray attenuation by matter. When the energy of the incident X-ray beam ($h\nu$) < binding energy (E_b) of a core electron on the element of interest, absorption is minimal. However, when $h\nu \approx E_b$, electron transitions to unoccupied bound energy levels arise, contributing the main absorption edge and causing features below the main edge, referred to as the preedge portion of the spectrum (Fig. 1.16). As $h\nu$ increases beyond E_b, electrons can be ejected to unbound levels and stay in the vicinity of the absorber for a short time with excess kinetic energy. In the energy region extending from just above to about 50 eV above E_b and the absorption edge, electrons are multiply scattered among neighboring atoms (Fig. 1.17a), which produces the XANES (X-ray absorption near edge structure) portion of the spectrum (Fig. 1.16). Fingerprint information, such as oxidation states, can be gleaned from this portion of the XAS spectrum. When $h\nu$ is about 50 to 1000 eV above E_b and the absorption edge, electrons are ejected from the absorber, singly or multiply scattered from first- or second-neighbor atoms back to the absorber, and then leave the vicinity of the absorber (Fig. 1.17b), creating the EXAFS (extended X-ray absorption fine structure) portion (Fig. 1.16) of the spectrum (Brown *et al.,* 1995). The EXAFS spectrum is caused by interference between outgoing and backscattered photoelectrons,

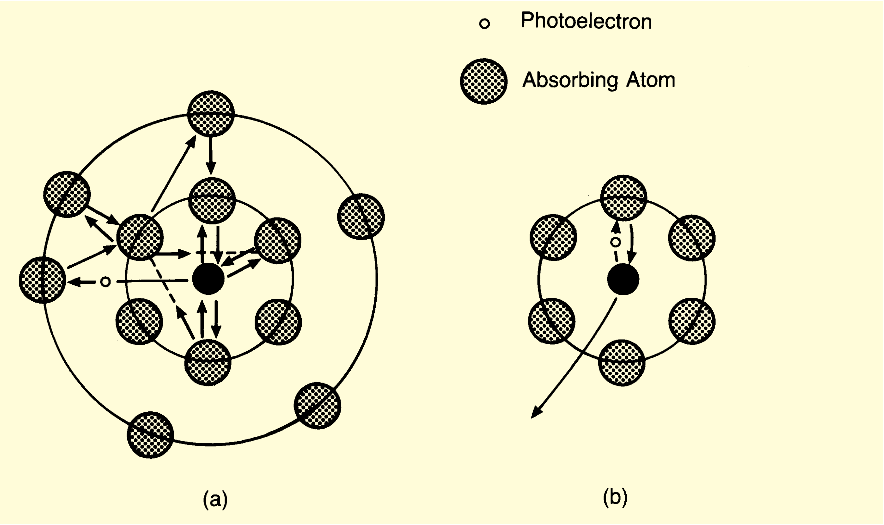


FIGURE 1.17. *Electron scattering process leading to (a) XANES and (b) EXAFS. From Brown et al. (1988), with permission. Copyright 1988 Springer-Verlag GmbH.*

which modulates the atomic absorption coefficient (Fig. 1.16). Analyses of the EXAFS spectrum provide information on bond distances, coordination number, and next nearest neighbors (Brown *et al.,* 1995).

XAS experiments can be conducted in several modes that differ in the type of detected particle: transmission (X-rays transmitted through the sample), fluorescence (fluorescent X-rays emitted due to absorption of the incident X-ray beam), or electron-yield (emitted photons). In a transmission experiment, the incident (I_0) and transmitted (I_1) X-ray intensities are recorded as a function of increasing incident X-ray energy (E) to yield an absorption spectrum, which is plotted as ln (I_0/I_1) vs E (in eV) (Fig. 1.16). The relationship between these intensities and the linear absorption coefficient μ (in cm^{-1}) of a sample of thickness x (in cm) is $\ln (I_0/I_1) = \mu x$. In a fluorescence experiment, the X-ray fluorescence from the sample, I_f, can be measured and ratioed with I_0 as I_f/I_0, which is proportional to μ for dilute samples. Fluorescence methods are preferred for elements that may be contained in low concentrations on mineral surfaces (Brown *et al.,* 1995).

The Lytle detector, which is a solid angle, gas-filled ion chamber detector, is frequently used in fluorescence experiments. Figure 1.18 shows the experimental apparatus for fluorescence XAS measurements using a Lytle detector. Samples are loaded into a mylar-windowed sample holder made of low Z materials (aluminum or Teflon).

The XANES region of the spectrum, while not providing as much quantitative information as the EXAFS region, is often more intense and can provide qualitative or semi-quantitative information on the oxidation state of the measured element (Brown *et al.,* 1995). Such information can be obtained by comparing the features of the XANES spectrum of the sample with features of XANES spectra for well-characterized reference compounds

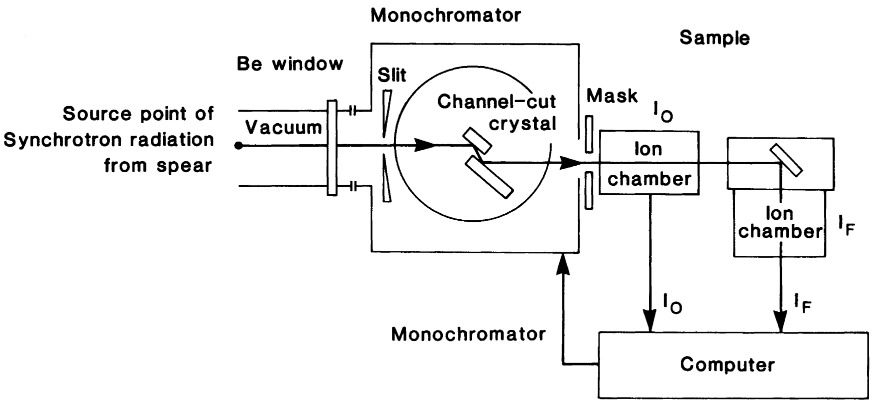


FIGURE 1.18. *Schematic illustration of the experimental setup used for fluorescence-yield XAS measurements. From Wong (1986), with permission.*

(Fig. 1.19). Some species, such as Cr, yield remarkably different, easily recognizable XANES spectra (Fig. 1.20). In Fig. 1.20 it is easy to differentiate Cr(III) from Cr(VI) as there is a prominent preedge feature for Cr(VI) that is absent for Cr(III).

Analysis of an EXAFS spectrum is illustrated in Fig. 1.21 and involves extracting structural parameters including interatomic distances (R), coordination numbers (CN), and identity of first, second, and more distant shells of neighbors around an absorber (Brown *et al.,* 1995).

To derive accurate structural parameters it is also necessary to obtain experimental EXAFS data for model or reference compounds that have known structures and contain the absorber and nearest-neighbor backscatters of interest. More detail on XAS methodology, sample preparation, and data analyses can be found in a number of excellent sources (Brown *et al.,* 1988, 1995; Brown, 1990; Fendorf and Sparks, 1996; Bertsch and Hunter, 1998; Fendorf, 1999; O'Day, 1999; Schulze and Bertsch, 1999).

Other Molecular-Scale Spectroscopic and Microscopic Techniques

As shown in Table 1.9, there are a number of *in situ* and *ex situ* analytical methods that are used in molecular environmental science.

The principal invasive *ex situ* techniques used for soil and aquatic systems are XPS, Auger electron spectroscopy (AES), and SIMS. Each of these techniques yields detailed information about the structure and bonding of minerals and the chemical species present on the mineral surfaces. XPS is the most widely used non-*in-situ* surface-sensitive technique. It has been used to study sorption mechanisms of inorganic cations and anions in soil and aquatic systems.

Examples of *in situ* techniques are ESR, FTIR, NMR, XAS, and Mössbauer spectroscopies.

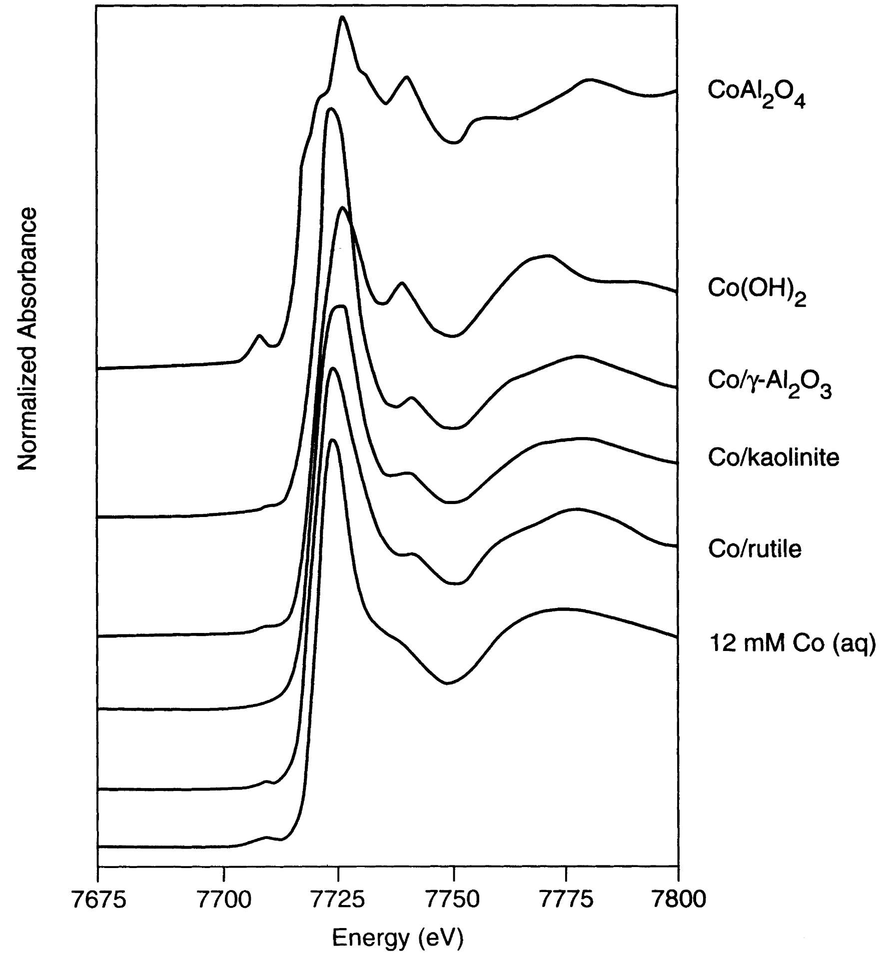


FIGURE 1.19. *Co K-edge XANES spectra of $CoAl_2O_4$ spinel, crystalline $Co(OH)_2$, three samples with aqueous Co(II) sorbed on γ-Al_2O_3, kaolinite [$Si_4Al_4O_{10}(OH)_8$], and rutile (TiO_2), and a 12 mM aqueous $Co(NO_3)_2$ solution. From Chisholm-Brause et al. (1990b). Reprinted with permission from Nature. Copyright 1990 Macmillan Magazines Ltd.*

ESR spectroscopy is a technique for detecting paramagnetism. Electron paramagnetism occurs in all atoms, ions, organic free radicals, and molecules with an odd number of electrons. ESR is based upon the resonant absorption of microwaves by paramagnetic substances and describes the interaction between an electronic spin subjected to the influence of a crystal field and an external magnetic field (Calas, 1988). The method is applicable to transition metals of Fe^{3+}, Cu^{2+}, Mn^{2+}, V^{4+}, and molybdenum (V) and has been used widely to study metal ion sorption on soil mineral components (McBride, 1982; McBride *et al.*, 1984; Bleam and McBride, 1986) and soil organic matter (Senesi and Sposito, 1984; Senesi *et al.*, 1985).

Application of IR spectroscopy to the study of soil chemical processes and reactions has a long history. The introduction of Fourier transform techniques has made a significant contribution to the development of new

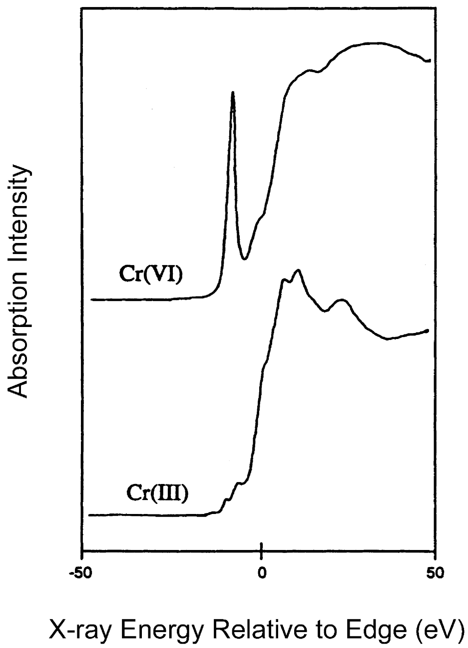


FIGURE 1.20.

Comparison of XANES spectra for Cr(III) and Cr(VI). From Fendorf et al. (1994c), with permission.

investigation techniques such as diffuse reflectance infrared Fourier transform (DRIFT) and attenuated total reflectance (ATR) spectroscopy. IR spectroscopy now extends far beyond classical chemical analysis and is applied successfully to study sorption processes of inorganic and organic soil components. These techniques, and other vibrational spectroscopies, such as Raman, are the subject of numerous reviews (Hair, 1967; Bell, 1980; McMillan and Hofmeister, 1988; Johnston *et al.,* 1993; Piccolo, 1994).

The use of NMR spectroscopy to study surfaces has a shorter history, and fewer applications than vibrational spectroscopies. The primary reason is that the sensitivity of NMR is much lower than that of IR. Properties that might be exploited are the chemical shift, NMR relaxation times, and magnetic couplings to nuclei that are characteristic of a surface (Wilson, 1987). Most NMR studies in the field of soil science concentrate on the characterization of soil organic matter and soil humification processes and, therefore, involve ^{1}H, ^{13}C, and ^{15}N NMR. Reviews on these and related topics are available (Wershaw and Mikita, 1987; Wilson, 1987; Johnston *et al.,* 1993; Hatcher *et al.,* 1994). Because it is virtually impossible to obtain any useful molecular information by observing the nucleus of a paramagnetic metal directly, studies of cation exchange have focused on diamagnetic metals, such as Cd^{2+}, which have a spin of $^{1}/_{2}$ and an acceptable natural abundance (e.g., 12 and 13%, respectively, for the two NMR-active isotopes, ^{113}Cd and ^{111}Cd). NMR is essentially a bulk spectroscopic technique. The advent of high-resolution, solid-state NMR techniques, such as magic angle sample spinning (MAS) and cross polarization (CP), along with more sensitive, high-magnetic-field, user-friendly, pulsed NMR spectrometers has brought increased applications

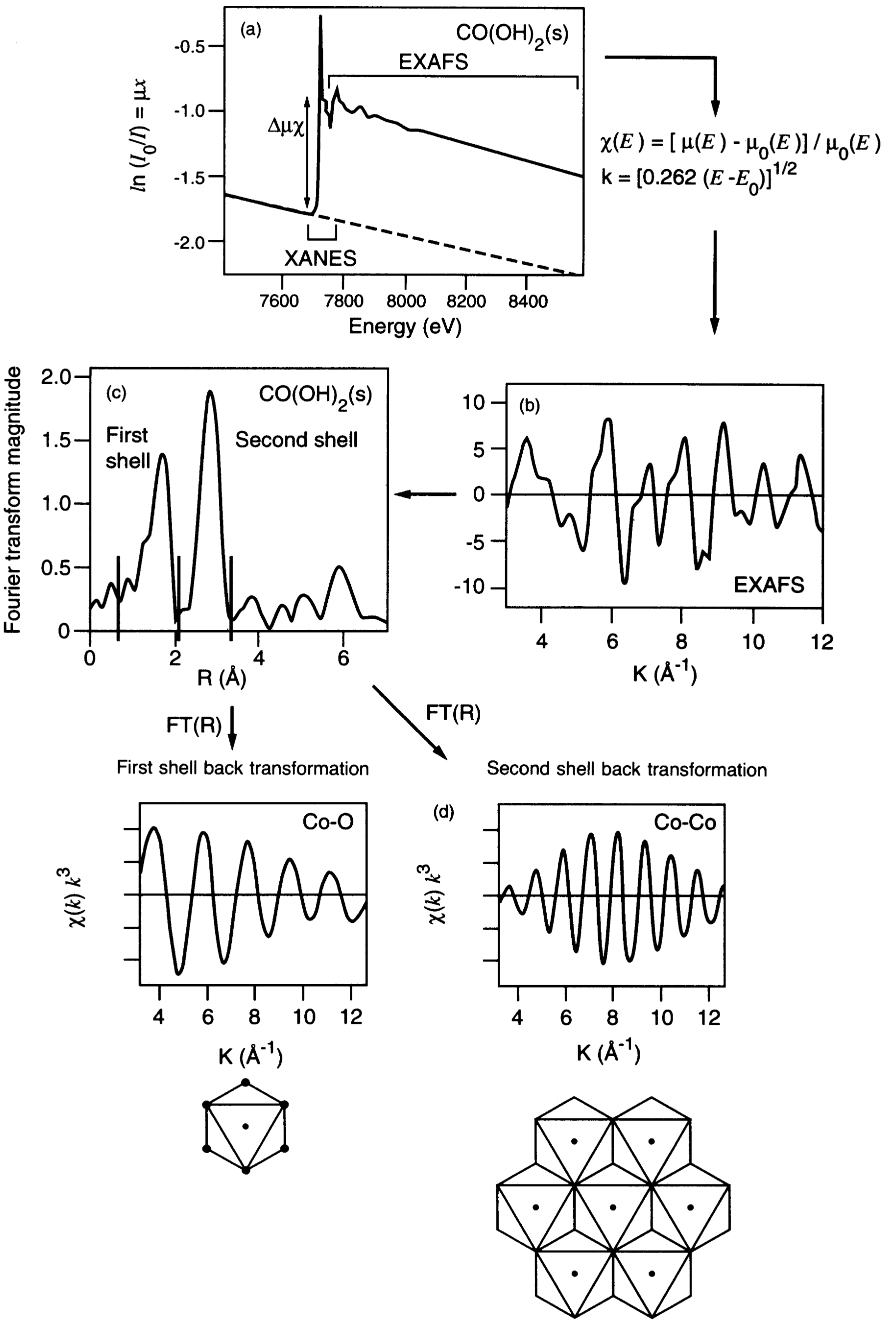


FIGURE 1.21. *Illustration of the steps involved in analysis of an EXAFS spectrum, using the Co K-edge XAS of solid* $Co(OH)_2$ *as an example. Subtraction of background (dashed line in the EXAFS spectrum) yields the EXAFS function* ($\chi(k) \times k^3$) *vs k* ($Å^{-1}$)*. Fourier transformation of the background-subtracted EXAFS function yields a radial structure function (Fourier transform magnitude vs R (Å)), which contains peaks at different distances associated with various shells of neighboring atoms around Co. Fourier filtering of the different shells and back Fourier transformation yields the frequency contribution of each neighboring shell of atoms around Co. In this example, the first peak in the radial structure function is caused by backscattering of the photoelectron from six nearest-neighbor O atoms at 2.08 Å from Co, and the second peak by backscattering from six second-neighbor Co atoms at 3.17 Å from the central Co atom (after O'Day, 1992).*

to heterogeneous aqueous systems (Johnston *et al.,* 1993). In particular, ^{27}Al and ^{29}Si NMR in zeolites and other minerals have proven valuable for the structural elucidation of samples whose disorder has prevented diffraction techniques from being very useful (Altaner *et al.,* 1988; Herrero *et al.,* 1989; Woessner, 1989).

Spatial information on soil chemical processes can be gleaned from microscopic analyses. Scanning electron microscopy, TEM, and HRTEM are well-established methods for acquiring both chemical and micromorphological data on soils and soil materials. TEM can provide spatial resolution of surface alterations and the amorphous nature or degree of crystallinity of sorbed species (ordering). It can also be combined with electron spectroscopies to determine elemental analysis.

From the very inception of the STM in 1981, it was apparent that this technique would revolutionize the study of mineral surfaces and surface-related phenomena. Indeed, by the end of the 1980s, applications of STM were beginning to appear in the earth sciences literature (Hochella *et al.,* 1989; Eggleston and Hochella, 1990). However, the major event for the environmental science community came with the development of SFM, also known as AFM. SFM allows imaging of mineral surfaces in air or immersed in solution, at subnanometer scale resolution (Maurice, 1996). SFM employs an atomic-sized tip positioned by a microcantilever and rastered over a surface (O'Day, 1999). Applications to date include determining the molecular-to-atomic scale structure of mineral surfaces (Johnsson *et al.,* 1991); probing forces at the mineral/water interface (Ducker *et al.,* 1992); visualizing sorption of hemimicelles and macromolecular organic substances such as humic and fulvic acid (Manne *et al.,* 1994; Maurice, 1996); determining clay particle thicknesses and morphology of clay-sized particles (Hartman *et al.,* 1990; Maurice *et al.,* 1995); imaging soil bacteria (Grantham and Dove, 1996); and measuring directly the kinetics of growth, dissolution, heterogeneous nucleation, and redox processes (Dove and Hochella, 1993; Junta and Hochella, 1994; Fendorf *et al.,* 1996). Excellent references on SFM methodology and applications can be found in a number of reviews (Hochella *et al.,* 1998; Maurice, 1998).

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